

AMERICAN CHEMICAL JOURNAL

[Contributions from the Sheffield Laboratory of Yale University]

CC.—HYDANTOINS

THE ACTION OF POTASSIUM THIOCYANATE ON ASPARAGINE¹

BY TREAT B. JOHNSON AND HERBERT H. GUEST

[FOURTEENTH PAPER]

It is well known that the amount of sulphur in many proteins is much greater than can be accounted for on the assumption that cystine and cysteine are the only sulphur combinations which are present in these natural substances. Regarding the nature of other sulphur linkings, we have practically no knowledge. Evidence is available,² however, which indicates that thioamide groupings functionate in the synthesis of sulphur proteins. In order, therefore, to obtain new data which we believed would contribute to our present knowledge of these substances, we took up the study of N-unsubstituted thiohydantoins. Several papers on these compounds have already been published³ and the investigation

¹ The work described in this paper formed part of a thesis presented by Mr. Herbert Hartley Guest to the Graduate School of Yale University for the degree of Doctor of Philosophy.

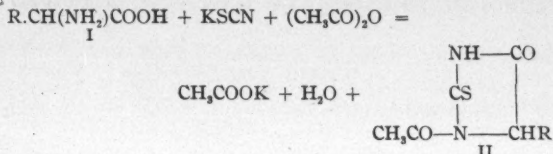
² Johnson: *J. Biol. Chem.*, **9**, 439.

³ *J. Biol. Chem.*, **10**, 139; **11**, 97. *J. Am. Chem. Soc.*, **33**, 1973. *THIS JOURNAL*, **47**, 242.

is still in progress. In this paper we shall describe some new thiohydantoin derivatives of aspartic acid.

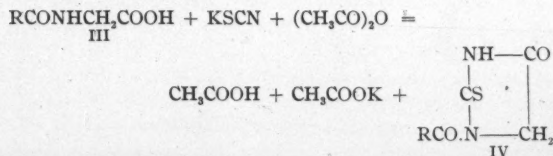
The N-unsubstituted thiohydantoins have been made by the application of an entirely new reaction, viz., by the action of potassium thiocyanate on α -amino acids in the presence of acetic anhydride. The results which we have obtained apparently permit us to make the two following statements:

(1) Monobasic α -amino acids (I) combine with potassium thiocyanate in acetic anhydride solution, forming 3-acetylthiohydantoins (II) according to the following equation:



Every α -amino acid which we have so far examined has reacted in this manner.

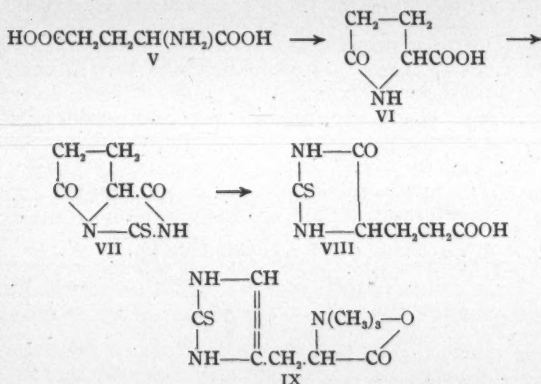
(2) α -Acylamino acids (III) react with potassium thiocyanate in acetic anhydride solution, forming the corresponding 3-acylthiohydantoins (IV) as follows:



This reaction has been applied only with hippuric and aceturic acids and acetylalanine, but we propose, as soon as possible, to test its general application with other acyl derivatives. The unsubstituted thiohydantoins are formed quantitatively by the hydrolysis of their 3-acyl derivatives with hydrochloric acid. The sulphur atom is not removed by this treatment.

While the reaction (I) can be applied successfully with the

monobasic amino acids, we were unable to obtain a thiohydantoin by the action of potassium thiocyanate on glutaminic acid.¹ This acid was deamidized under these conditions and in order to synthesize the hydantoin we started with pyrrolidonecarboxylic acid (VI) and applied Method (2). This acid combined smoothly with potassium thiocyanate, forming the bicyclic derivative (VII), which then underwent a normal hydrolysis with acids, giving the 2-thiohydantoin-4-propionic acid (VIII). The corresponding hydantoin derivative has been prepared by Dakin.² This thiohydantoin derivative (VIII) is of interest because of its relationship to *ergothioneine* (IX), which Tanret isolated from ergot of rye.³ These various changes are represented by the following formulas:



We have now made the interesting observation that aspartic acid (X) likewise reacts abnormally with potassium thiocyanate in acetic anhydride solution. It behaves in the same manner as glutaminic acid and is deamidized. In other words, the presence of the two carboxyl groups in these two

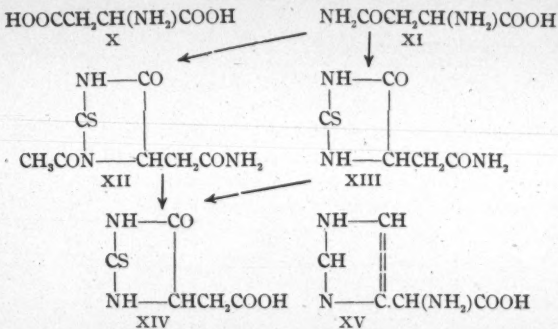
¹ Johnson and Guest: *THIS JOURNAL*, **47**, 242.

² *Ibid.*, **44**, 48.

³ *J. pharm. chim.*, **30**, 145. *Compt. rend.*, **149**, 2222. Barger and Ewin: *J. Chem. Soc.*, **1911**, 2336.

acids apparently prevents the formation of thiohydantoin by the action of potassium thiocyanate. On the other hand, if the influence of one of the carboxyls is destroyed a thiohydantoin is formed almost quantitatively.

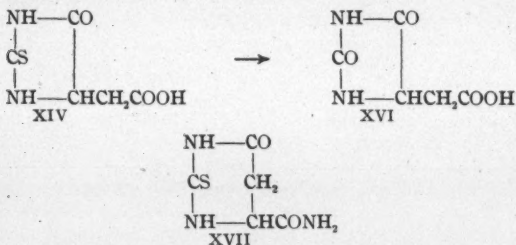
We now find that the thiohydantoin (XIV) can be obtained from asparagine (XI). This amide reacts normally with potassium thiocyanate according to Reaction (I), forming the acetylthiohydantoin (XII). The latter was then converted into the thiohydantoin of aspartic acid (XIV) by hydrolysis with hydrochloric acid. A secondary product of this reaction was 2-thiohydantoin-4-acetamide (XIII), which also gave on hydrolysis the thiohydantoin (XIV):



The structure of the thiohydantoin (XIV), and incidentally those of the hydantoin (XII) and (XIII), was established as follows: It was desulphurized when digested with chloroacetic acid, forming quantitatively the corresponding hydantoinacetic acid (XVI), whose constitution was definitely established by Gabriel.¹ This formation of a thiohydantoin derivative from asparagine is therefore a new proof that the CONH₂ group in this acid is joined to a different carbon than the amino radical. The isomeric derivative would be expected

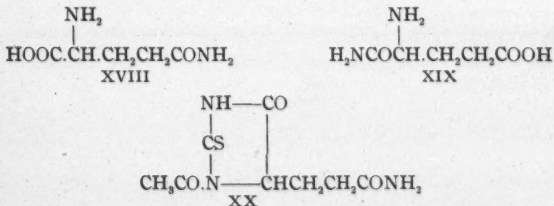
¹ Ann. Chem. (Liebig), 348, 89.

to combine with potassium thiocyanate and form a hexahydro-pyrimidine (XVII):



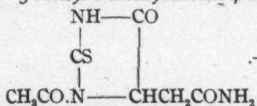
2-Thiohydantoin-4-acetic acid (XIV) is of particular interest because it has the same relation to aminoimidoazole-acetic acid (XV) as 2-thiohydantoin-4-propionic acid (VIII) has to histidine. Engeland¹ claims to have isolated this glyoxaline derivative (XV) from human urine in the form of its picrolonate, $\text{C}_5\text{H}_7\text{O}_2\text{N}_3 \cdot \text{C}_{10}\text{H}_5\text{O}_5\text{N}_4$.

So far as the writer is aware, the constitution of glutamine has never been established. If this amide is to be assigned the structure (XVIII) corresponding to that of asparagine, then theoretically it should react with potassium thiocyanate with formation of a thiohydantoin derivative (XX). The writer hopes that some investigator, to whom this rare substance is available, will try this reaction and establish the constitution of this naturally occurring amino acid.



¹ Z. physiol. Chem., **87**, 49.

EXPERIMENTAL PART

*The Action of Potassium Thiocyanate on Asparagine**3-Acetyl-2-thiohydantoin-4-acetamide,*

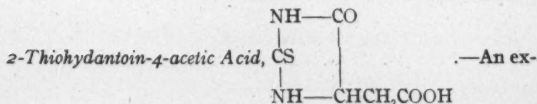
.—Two grams of anhydrous aspar-

agine (Kahlbaum's) and 1.5 grams of a carefully dried potassium thiocyanate were ground together to a fine powder and then suspended in 9 cc. of acetic anhydride to which 1 cc. of glacial acetic acid was added. The mixture was then heated on the water bath for 30 minutes. There was a slight effervescence and a clear, yellow solution was obtained. This was cooled and poured into 50 cc. of cold water, when this hydantoin separated in slender, prismatic crystals. The compound is readily soluble in hot but difficultly soluble in cold water and easily soluble in alcohol. It melts at 222° – 223° with effervescence. The yield was 1.8 grams. Analysis (Kjeldahl):

	Calculated for $\text{C}_7\text{H}_9\text{O}_3\text{N}_3\text{S}$	Found
N	19.53	19.3

In another experiment, in which we used 10 grams of asparagine, the thiohydantoin separated from the acetic anhydride solution after cooling to 0° . In this manner we obtained 7.2 grams of the thiohydantoin. The acetic anhydride filtrate was then diluted with 200 cc. of water. No more thiohydantoin separated. The solution was then concentrated to a small volume at 100° and cooled, when *2-thiohydantoin-4-acetamide* separated. This was purified by recrystallization from hot water and melted at 246° with effervescence. Analysis (Kjeldahl):

	Calculated for $\text{C}_6\text{H}_7\text{O}_2\text{N}_3\text{S}$	Found
N	24.2	24.4



celleat yield of this compound is obtained by hydrolysis of the above acetylthiohydantoin. Two grams of 3-acetyl-2-thiohydantoin-4-acetamide were digested for about one hour with hydrochloric acid. The acid solution was then concentrated to about one-half its original volume and cooled, when this thiohydantoin separated. It was purified for analysis by crystallization from hot water and deposited, on cooling, in hexagonal tables or plates, which melted at 222° with decomposition. The hydantoin is more soluble in alcohol than in water. A mixture of this compound with 3-acetyl-2-thiohydantoin-4-acetamide melted at 195° – 198° .

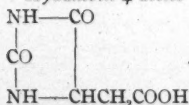
Carbon and nitrogen determinations:

I. 0.1145 gram substance gave 0.1430 gram CO_2 and 0.0400 gram H_2O .

Nitrogen determination (Kjeldahl):

	Calculated for $\text{C}_8\text{H}_6\text{O}_2\text{N}_2\text{S}$	I	Found	II
C	34.4	34.06	...	...
H	3.4	3.9	...	...
N	16.1	16.13	16.22	...

Hydantoin-4-acetic Acid (Malyureidic Acid),



—This hydantoin was obtained by the

desulphurization of 2-thiohydantoin-4-acetic acid. This was accomplished as follows: Two grams of 2-thiohydantoin-4-acetic acid were digested for 3 hours with 2 grams of chloroacetic acid dissolved in 10 cc. of water. The hydantoin dissolved on warming, giving an almost colorless solution. This was evaporated to dryness and the hydantoin purified by crystallization from boiling alcohol or water. It deposited, on cooling, in blocks. After repeated recrystallizations from alcohol the acid melted constant at 214° – 215° in an open capillary tube. It did not give a test for sulphur. Analysis (Kjeldahl):

	Calculated for $\text{C}_8\text{H}_6\text{O}_4\text{N}_2$	Found
N	17.7	17.5

This same hydantoin has been obtained by Grimaux,¹ Guareschi,² Gabriel,³ Lippich,⁴ and Dakin.⁵ These authors record various melting points from 207°-228°. These irregularities are probably due to mixtures of the active and racemic modifications. Dakin states that the pure inactive hydantoin melts at 225°-228°, first slightly sintering. It has been our experience that the decomposition point of this compound is indefinite and depends upon the mode of heating. An attempt to desulphurize 2-thiohydantoin-4-acetic acid by digestion with mercury oxide was not successful. For example, one gram of the thiohydantoin and an excess of moist mercury oxide were digested in water for about one hour. Mercury sulphide was formed and some mercury dissolved. After treatment with hydrogen sulphide to decompose any soluble mercury compounds and filtering, the solution was then evaporated to dryness. A semisolid residue was obtained, but no definite product was isolated. The hydantoin was apparently oxidized by the oxide.

The Action of Potassium Thiocyanate on Aspartic Acid

While asparagine reacts with potassium thiocyanate, aspartic acid does not combine smoothly with this reagent to form the corresponding hydantoin acid. The results obtained by us show that aspartic acid is deamidized by the action of potassium thiocyanate in acetic anhydride solution. We performed several experiments, using 2 grams of aspartic acid, 1.5 grams of the thiocyanate, 9 cc. of acetic anhydride and 1 cc. of acetic acid in each case. In only one experiment did we obtain any evidence of the formation of a 2-thiohydantoin derivative and then it was formed in so small an amount that it could not be purified. In order to explain this behavior we performed the following experiment:

The same proportions of acid, thiocyanate and anhydride were taken as described above and the mixture heated for 30

¹ Ann. chim. phys., [5] 11, 402 (1877). Compt. rend., 81, 325. Bull. soc. chim., [2] 24, 337.

² Beilstein's Handbuch, I, 1383.

³ Ann. Chem. (Liebig), 348, 87.

⁴ Ber. d. chem. Ges., 41, 2972, 2981.

⁵ THIS JOURNAL, 44, 57.



Plate I

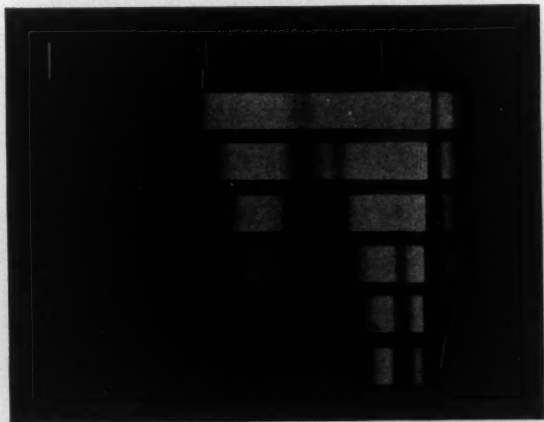


Plate II

minutes. There was a brisk evolution of gas and a clear yellow solution was obtained. This was cooled, diluted with an excess of dilute hydrochloric acid and the solution then evaporated to remove the excess of acid. A syrupy residue was obtained, which was transferred to a Kjeldahl flask, an excess of sodium hydroxide solution added, and the mixture then distilled. The distillate was collected in a beaker containing an excess of hydrochloric acid. After about 400 cc. had distilled over, the acid solution was then evaporated to dryness and the ammonium chloride dried and weighed. The results are given in the following table:

	Gram
NH ₄ Cl equivalent to N in aspartic acid	0.80
NH ₄ Cl equivalent to N in KSCN	0.80
Total NH ₄ Cl available	1.60
NH ₄ Cl obtained	1.30

In other words, over 80 per cent. of the nitrogen was recovered in the form of ammonium chloride. It is evident therefore, that the aspartic acid is deamidized and a thiohydantoin is not formed. 2-Thiohydantoin-4-acetic acid can be digested with dilute hydrochloric acid without decomposition.

NEW HAVEN, CONN.
May 27, 1912

METHODS FOR DETERMINING NEO- AND ALLO- CHLOROPHYLL IN THE PRESENCE OF ONE ANOTHER

By C. A. JACOBSON AND L. MARCHLEWSKI

In our previous paper¹ we showed that the ratio of neo-chlorophyll to allochlorophyll in plants is not a constant one. This ratio is not only variable in different species of plants but may show variations in the same species, where the samples have been grown under different conditions.

Plant physiology and the study of the functions of chlorophyll have been greatly handicapped for the want of a suffi-

¹ THIS JOURNAL, 47, 221.

ciently exact method for determining the ratio of the two components of this substance when present in small quantities of the green material.

Tswett¹ endeavored to work out a method which was based on the adsorptive properties of calcium carbonate for the two coloring matters. By this method he came to the conclusion that neo- and allochlorophyll are present in a constant proportion in all plants, which, in the light of more recent work, is manifestly erroneous.

In our work with various kinds of leaves we noticed the marked difference which the ultraviolet spectra presented. Nettle and *Acer negundo*, for example, were fundamentally different in this respect. A study of these varieties, together with the spectrum of allochlorophyllan, led us to surmise that the band characterized by wave lengths $\lambda = 436.5-442.8$ was entirely due to the latter substance, whereas the band in the region $\lambda = 391.8-399.7$ was produced by neochlorophyllan; but since we did not have this substance in a pure state, a positive statement could not be made. We noticed, further, that only minute quantities of material are necessary for producing these absorption bands so that we directed our efforts for obtaining the desired method along this line, but it is obvious that the success of our attempts would depend upon whether or not we could prepare neochlorophyllan in pure condition.

This we succeeded in doing by two entirely different methods. The one starting with chlorophyllan, the first acid derivative of chlorophyll, is the shorter and less cumbersome and will therefore be given precedence.

Method 1.—Two grams chlorophyllan, obtained as described in our previous paper, were dissolved in a liter of ether and shaken vigorously together with 200 cc. concentrated hydrochloric acid for a few minutes in a separatory funnel, during which time the funnel was cooled under the water tap. The liquids were allowed to separate, after which the acid portion was drawn off and shaken with two successive 250 cc. portions of ether. By this treatment the phylloxanthin was removed,

¹ Ber. d. bot. Ges., 24, 384 (1908).



Plate III



Plate IV

leaving the neochlorophyllan in the acid. The acid portion was then poured into 2 liters of water and extracted with one liter of ether. The ether solution thus obtained was shaken with 250 cc. of 10 per cent. hydrochloric acid and the liquids allowed to separate. The acid had only a slight color, but after the next extraction with 1 liter of 15 per cent. hydrochloric acid the latter was deeply colored dark blue by reflected and bluish purple by transmitted light. The 15 per cent. hydrochloric acid served to remove the phyllocyanin that was formed from the neochlorophyllan by the action of the concentrated acid. This treatment was repeated once or twice, after which the ethereal solution was extracted with an equal volume of 20 per cent. hydrochloric acid and this shaking repeated two or three times until the acid separated with only a slight yellowish green color. The ether was then freed entirely from acid by successive washings with water, after which the ether was distilled off and the resulting neochlorophyllan taken up in chloroform and precipitated with alcohol in the ordinary way. Neochlorophyllan is a black, amorphous substance, having an odor suggesting oak bark. In solution it has a deep olive-green color and is easily distinguishable from a solution of allochlorophyllan, which has a reddish brown color. In the following table will be found the measurements of the five absorption bands of neochlorophyllan in the visible part of the spectrum.

Plate I represents a photograph of the absorption bands of this substance in the visible spectrum, the solvent, concentration and thickness of layers being the same as those given in the above table. Five absorption bands are seen which are essentially the same as those described for nettle chlorophyllan, with the exception that the fourth band of the neochlorophyllan is narrower and better defined. In the 3- and 5-mm. layers we noticed light streaks in the centre of the first and fifth bands, and these can be seen in the negatives but are lost in the prints and reproductions. We also noticed a faint shading which was only a suggestion of a sixth band located between the blue and violet part of the spectrum. In ethereal solu-

Table I.—Spectrum of *Neochlorophyllan*

Concentration: 0.0004 gram per cc. chloroform

Thickness of layer Band	Concentration: 0.0004 gram per cc. chloroform				
	1.5 mm.	3 mm.	5 mm.	7 mm.	
I	λ 676.5-660.2	λ 680.5-656.0	λ 685.2-654.0	λ 687.7-650.5	
II	λ 613.4-600.3	λ 615.0-600.7	λ 616.4-599.8	λ 617.7-599.4	
III			λ 567.7-558.2	λ 568.1-558.2	
IV	λ 541.2-532.7	λ 541.5-533.0	λ 543.1-532.7	λ 543.7-531.6	
V	λ 513.0-499.2	λ 513.8-497.7	λ 514.5-496.5	λ 514.7-496.2	

Thickness of layer Band	Concentration: 0.0004 gram per cc. chloroform		
	9 mm.	11 mm.	
I	λ 690.0-647.4	λ 692.0-621.8	
II	λ 620.8-598.6	λ 621.4-595.5	
III	λ 570.2-556.2	λ 571.2-555.6	
IV	λ 545.0-531.6	λ 545.7-529.8	
V	λ 515.9-494.4	λ 517.3-493.9	

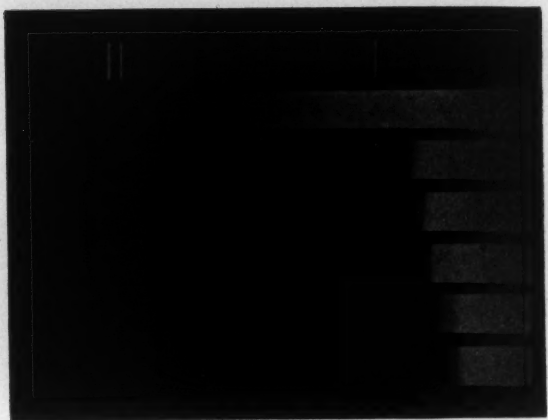


Plate V

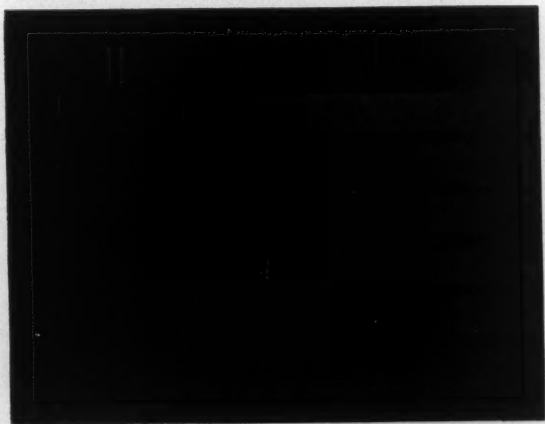


Plate VI

tions this band comes out stronger and could be measured with some degree of accuracy.

The ultraviolet spectrum of neochlorophyllan is, however, by far the more interesting and serves as the basis for the present method of determining the two coloring matters in the presence of one another. Plate IV represents the ultraviolet spectrum of neochlorophyllan obtained by the foregoing method. The plate shows only three absorption bands, which are recorded in wave lengths in the following table. The readings were taken from the negative in correlation to the lines of the copper spectrum, while the helium lines furnished the fixed points for the measurements in the visible portion.

Table II.—Neochlorophyllan Spectrum

Concentration: 0.00004 gram per cc. chloroform

Thickness of layer mm.	Band III	Band II	Band I
2		λ 394.0-403.0	λ 409.6-421.3
4	λ 366.4-381.3	λ 391.0-404.1	λ 408.4-424.0
6	λ 365.0-382.7	λ 388.8-405.0	λ 407.4-426.5
8	λ 364.0-383.8	λ 387.2	428.8
10	λ 361.5		430.5
12	λ 357.4		432.5

By comparing the above readings with those obtained for nettle, *Platanus occidentalis* or any other of the chlorophyllans measured and recorded in our previous paper, the neochlorophyllan bands may be easily located.

From the work of Marchlewski and Marszalek¹ we learn that the chlorophyllan obtained from the leaves of *Acer platanoides* (1910) had a phytol content of 34.24 per cent., whereas the allochlorophyllan separated from that mixture contained only 30.75 per cent. when the substance was dried in a vacuum desiccator or 32.85 per cent. after drying at 105°. The same experimenters also found that the methoxyl contained in the above-mentioned chlorophyllan amounted to 3.44 per cent., whereas the corresponding allochlorophyllan yielded only 3.15 per cent.; it was interesting to know what values would be obtained in the case of neochlorophyllan.

¹ Biochem. Z., **38**, 413 (1911).

The following are the results obtained from this substance, isolated and purified by the method already described. The phytol was dried to constant weight in a vacuum desiccator over sulphuric acid:

1.6462 grams neochlorophyllan gave 0.5480 gram phytol, or 33.3 per cent.

0.3191 gram neochlorophyllan gave 0.0796 gram AgI, or 3.29 per cent. OCH_3 .

We also wish to present the second method by which neochlorophyllan was obtained in pure condition, and this is especially significant for the reason that the product is extracted directly from the leaves by means of organic solvents alone. No acids or alkalis were used at any stage of the process, except at the end, when the pure neochlorophyll was converted into its acid derivative.

Making use of the results of Sorby¹ and Marchlewski and Schunck² for the preparation of pure chlorophyll we finally developed a method which led to the desired result.

Method 2.—Three liters of cold 92 per cent. alcohol were poured on 1 kilogram of dried and finely ground *Acer platanoides* leaves and the mixture allowed to stand for one hour, after which the alcoholic extract was pressed out under 300 atmospheres. The filtered extract showed an extinction coefficient for sodium light of 6.32. One liter of this extract was shaken with 100 cc. petroleum ether and allowed to stand. Twenty-five cc. of water were added to make the liquids separate more quickly. After letting off the alcoholic portion, this was shaken with 800 cc. carbon disulphide. The latter solvent was then separated, measuring 850 cc., which was in turn shaken with an equal volume of 82 per cent. alcohol. A few cc. of 95 per cent. alcohol were added to facilitate the separation. This shaking with 82 per cent. alcohol was carried out three successive times, after which 365 cc. carbon disulphide solution remained. The latter was then shaken with an equal volume of 85 per cent. alcohol. From this mixture 240 cc. carbon disulphide solution separated, which was

¹ P. Roy. Soc., **21**, 442 (1873).

² J. Chem. Soc., **77**, 1080 (1900).



Plate VII

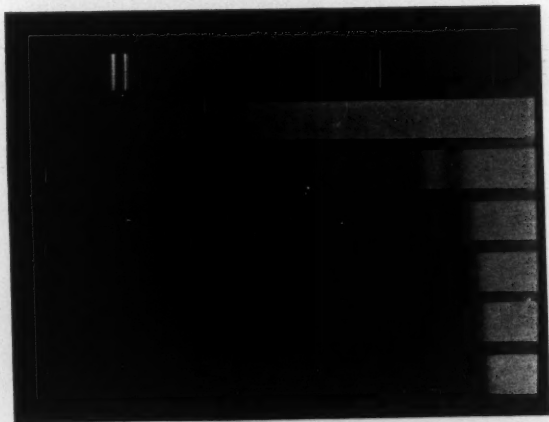


Plate VIII

in turn shaken with an equal volume of 87 per cent. alcohol. From this shaking only 165 cc. carbon disulphide solution remained, but this was made up to 200 cc. with carbon disulphide and then shaken with 200 cc. of 87 per cent. alcohol. These extractions with 87 per cent. alcohol were repeated seven successive times. The carbon disulphide portion was then treated in like manner with 90 per cent. alcohol six times, and finally with 92 per cent. alcohol five times, making twenty-five extractions in all. At every stage of the operation we were guided by the spectroscope. As pointed out in our former paper, the position of the first band of neochlorophyllan in dilute solution is not identical with that of allochlorophyllan and the same is true for the primal substances. The shading on the more refrangible side of this band is due to the allochlorophyll and in this way we could follow the course of the extraction. The neochlorophyll remained in the carbon disulphide solution, whereas the allochlorophyll was removed gradually by the alcoholic extracts.¹ The last carbon disulphide portion was evaporated to dryness on a water bath and the residue taken up in alcohol, filtered, treated with a 10 per cent. alcoholic solution of oxalic acid, and after standing for some hours the neochlorophyllan was filtered off and washed. Plate III represents a photograph of neochlorophyllan in the ultraviolet, obtained by the method just described. Although the prints and reproductions of the spectra of the two neochlorophyllans obtained by different methods are identical yet upon closely scrutinizing the negatives it will be found that the negative of the latter contains a very faint trace of a band in the region of the copper line $\lambda = 437.8$, showing that a trace of allochlorophyllan still remained. The above process was repeated and the extraction with 92 per cent. alcohol carried on a little further, which removed the allochlorophyll altogether. The above establishes that it is possible, by means of organic solvents alone, to separate the two green coloring

¹ It will be seen that the method here described is far more complicated than the one used by Marchlewski and C. A. Schunck (*loc. cit.*). The *Acer platanoides* evidently contained much more of the allochlorophyll than *Ficus repens* used by the authors named. The great difference in the composition of green leaves met with, not only in case of the green, but also of the yellow coloring matters, makes it necessary to change the original method of Sorby according to circumstances.

matters in leaves and to obtain at least one of them in pure condition. Plate II gives the visible spectrum of neochlorophyllan obtained by the method just described and is identical in every detail with Plate I. A few per cent. of allochlorophyllan can, however, be detected in the visible spectrum, when mixed with the neo compound, but the present work has brought out that for the chlorophylls the ultraviolet region is far more delicate.

In our effort to obtain a method for determining one of these coloring matters in the presence of the other we have made use of this fact, and have photographed artificial mixtures of neo- and allochlorophyllan having the following compositions:

Table III

Plate	Neochlorophyllan		Allochlorophyllan	
	IV	100 per cent.		0 per cent.
"	V	90	"	+ 10 "
"	VI	80	"	+ 20 "
"	VII	70	"	+ 30 "
"	VIII	60	"	+ 40 "
"	IX	50	"	+ 50 "
"	X	40	"	+ 60 "
"	XI	30	"	+ 70 "
"	XII	20	"	+ 80 "
"	XIII	10	"	+ 90 "
"	XIV	0	"	100 "

A much larger series of photographs could, of course, have been made, thus making the range for estimation smaller, but from the present series it is certainly possible to determine the composition of a mixture to within two per cent. from the prints, and less than that from the negatives.

The method is then to prepare the chlorophyllan from any plant in the ordinary way, being careful to remove all the yellow coloring matters by means of several precipitations with alcohol from concentrated chloroform solutions and to make a solution whose concentration is equal to those photographed in the series, or 0.00004 gram per cc., and then to take a photograph in the ultraviolet, with the same thickness of layers, i. e., 2, 4, 6, 8, 10 and 12 mm. A direct comparison of



Plate IX

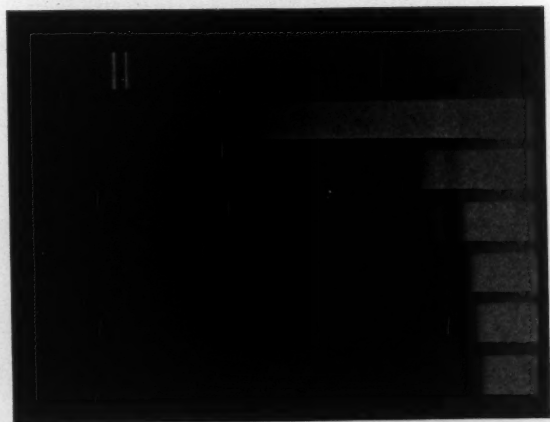


Plate X

the photograph with those given in this series will reveal the composition.

An experiment was carried out to ascertain if the yellow coloring matters of the leaves exert an influence on the chlorophyllan bands in the ultraviolet in such small concentrations. To this end 1 liter of alcoholic extract of *Acer platanoides* was divided into two equal portions. One was treated with 15 cc. of 10 per cent. alcoholic oxalic acid and allowed to stand overnight. Calcium carbonate in excess of the oxalic acid was then added, to prevent the formation of phyllocyanin, and the solution evaporated to dryness on the water bath. The residue was extracted with chloroform until the brown color was removed. The chloroform solution measured 302 cc. One cc. of this solution was diluted with chloroform to 60 cc., which was approximately our standard concentration, and the solution photographed in the ultraviolet. It gave a normal chlorophyllan spectrum. To the other portion was added 25 grams solid potassium hydroxide and the solution allowed to stand for two hours with frequent stirring. The solution was then evaporated to a syrup, at a low temperature, on the water bath, after which water was added and the aqueous solution extracted with ether in a separating funnel. Six shakings with ether were required before the latter separated colorless. The ether was distilled off and the yellow coloring matters dissolved in chloroform, filtered and made up to the same volume as the chlorophyllan in the first part of the experiment. The same volume concentration of the yellow coloring matters was then photographed in the ultraviolet. This resulted in a blank negative.

We have thus established that the yellow coloring matters in leaves, the carotin and xanthophylls, do not influence the chlorophyllan bands in the ultraviolet in the proportion in which the two are present in *Acer platanoides* leaves. If this were the case in all other varieties of leaves the method of determining the ratio of neo- to allochlorophyll could be much simplified. It would only be necessary to acidulate the alcoholic extract of the material with oxalic acid, to neutralize the excess of the acid by adding calcium carbonate, to evapo-

rate the solution to dryness, extract the residue with chloroform and to take a series of photographs in the ultraviolet.

The second method for determining the ratio of neo- to allochlorophyllan in mixtures of the two is based on the extinction coefficients of the chloroform solutions. This method has already been applied by Marchlewski and Malarski¹ for determining the total green coloring matter in a given plant. We have already called attention to the difference existing in the green part of the spectrum of neo- and allochlorophyllan and have recorded the extinction coefficients of nettle, *Platanus occidentalis* and *Acer negundo* chlorophyllans, obtained by means of a monochromator, but in that case the light was only approximately monochromatic. For the present work we employed a cadmium lamp giving true monochromatic light in this region of the spectrum. The extinction coefficients were obtained of the same mixtures of neo- and allochlorophyllan as were photographed in the series beginning with neo- and ending with allochlorophyllan. The same spectrophotometer and method for calculating the results were employed as described in our previous paper, to which reference has already been made.

Table IV.—Extinction Coefficients of Artificial Mixtures
Concentration: 0.0004 gram in 1 cc. (chloroform)

Neochlorophyllan	Allochlorophyllan	Cd light $\lambda = 508 \mu\mu$	Na light $\lambda = 589 \mu\mu$
100 per cent.	0 per cent.	4.38	1.22
90 "	+ 10 "	4.24	1.34
80 "	+ 20 "	4.14	1.42
70 "	+ 30 "	3.99	1.52
60 "	+ 40 "	3.90	1.61
50 "	+ 50 "	3.80	1.68
40 "	+ 60 "	3.70	1.76
30 "	+ 70 "	3.54	1.85
20 "	+ 80 "	3.41	1.97
10 "	+ 90 "	3.33	2.07
0 "	100 "	3.21	2.16

The above results, obtained with the cadmium light, are represented in the following figure and it will be seen that the curve, barring experimental errors, is a straight line.

¹ Biochem. Z., 24, 319.

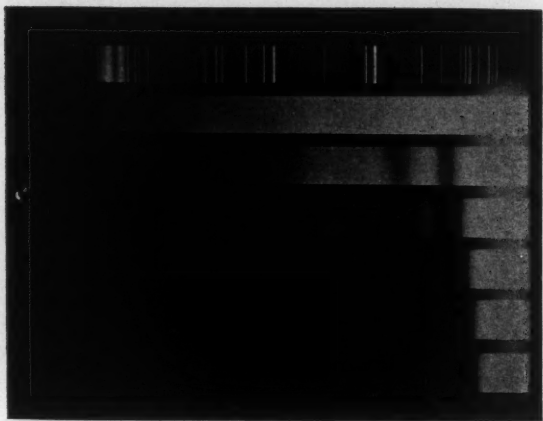


Plate XI



Plate XII

By closely observing the spectra of the two substances in the visible portion it will be seen that the second band of allochlorophyllan extends slightly further in the direction of the more refrangible end than that of the neo compound, so that the edge of the allochlorophyllan band just overlaps the sodium

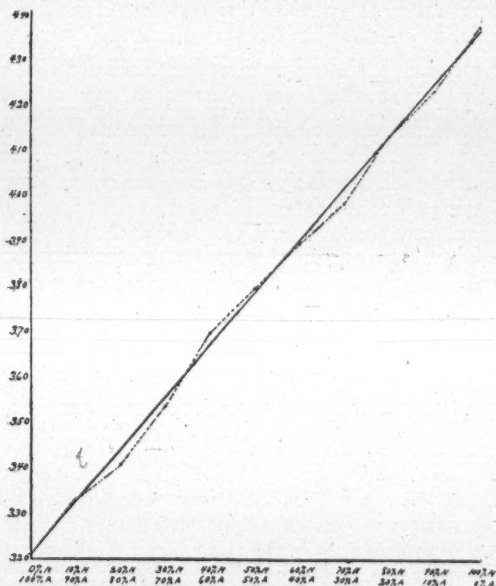


Fig. I

line, while the edge of the neo band does not quite reach it. Consequently we ought to find the reverse arrangement of the extinction coefficients for the above mixtures when sodium light is employed. Our results, given in Table IV, obtained with the sodium light, are embodied in Fig. II, which is self-explanatory. The ordinates of the curves are the extinction

coefficients and the abscissas the percentage composition. *N* represents neochlorophyllan and *A* allochlorophyllan

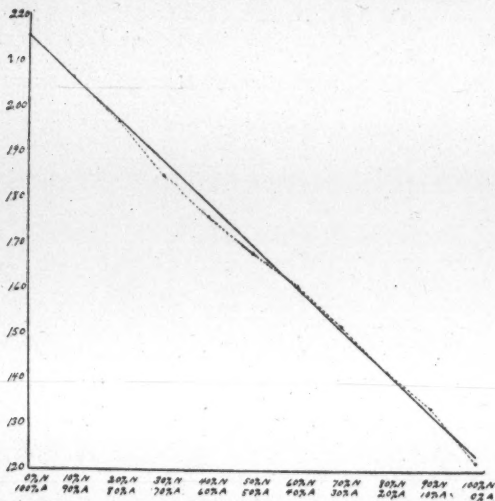


Fig. II

Also in this case it is seen that the percentage composition of any mixture of neo- and allochlorophyllan is a linear function of its extinction coefficient.

The extinction coefficients, either in cadmium or sodium light, therefore furnish a delicate method for determining the ratio of neo- to allochlorophyllan in an unknown mixture, provided the chlorophyllan has been well purified and the concentration standardized with great care. The photographic method is not so sensitive to impurities and is therefore more adapted to practical application.

Chloroform solutions of the following varieties of chlorophyllans have been employed to illustrate the present photo-

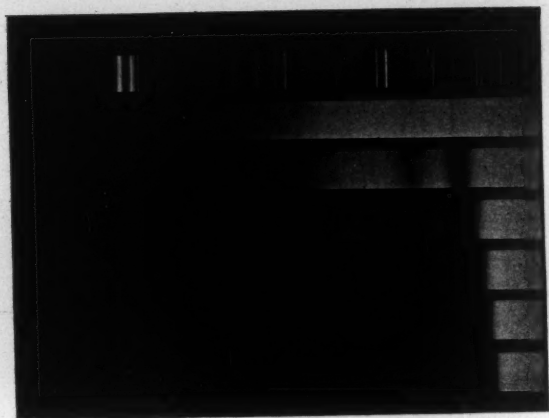


Plate XIII

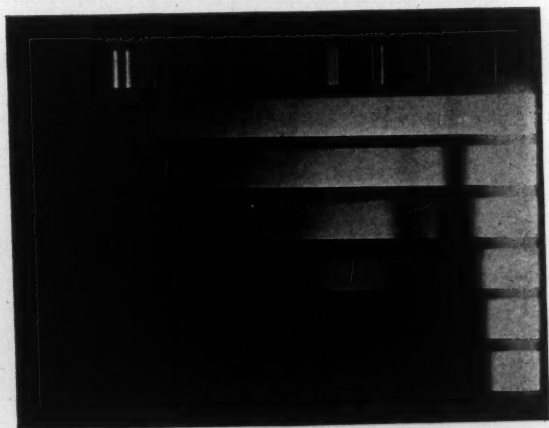


Plate XIV

graphic method of determining the two components. The solutions used, however, have been standing for more than three months, and some have undoubtedly changed in concentration during the time, so we should not expect to find the method by the extinction coefficients to give concordant results, since the curves are made from freshly prepared solutions. The time at our disposal was too short to prepare new solutions of different varieties. A slight change in concentration does not influence the photographic method a great deal because ten times more dilute solutions are employed and the relative intensity of the absorption bands would not be appreciably influenced. The same volume concentration and thickness of layers were used for the unknown solutions as for those in the series. The results were found to be as follows:

Table V

	Neochlorophyllan Per cent.	Allochlorophyllan Per cent.
Nettle (Plate IX of our first series)	72	28
<i>Acer negundo</i> (Plate VI)	12	88
<i>Platanus occidentalis</i> (Plate VIII)	40	60
<i>Acer campestre</i>	58	42
<i>Isatis tinctoria</i>	65	35
<i>Acer pseudo-platanus purpur.</i>	43	57
Fern	63	37
<i>Galeopsis tetrahyt</i>	60	40

In two cases we were able to test the above results by the extinction coefficient method. The *Isatis tinctoria* chlorophyllan gave a coefficient for Cd light of 3.98; by interpolation, using the absorption curve, Fig. I, we find 66 per cent. neochlorophyllan and 44 per cent. allochlorophyllan. The nettle chlorophyllan gave $E = 4.01$, corresponding to 69 per cent. neo- and 31 per cent. allochlorophyllan.

It is then seen that we have here two methods applicable for determining the ratio of the components of chlorophyll. The photographic method can be used when only very small quantities of material are available. Having the comparison series of spectrographs, the determination is easily and quickly made.

The extinction method is more sensitive to colored impurities, but where the quantity of chlorophyll is large enough so that it can be sufficiently purified, this method allows of greater accuracy.

POTENTIALS OF ZINC IN ALCOHOLIC SOLUTIONS OF ZINC CHLORIDE

BY FREDERICK H. GETMAN AND VERNETTE L. GIBBONS

In a previous communication¹ it was pointed out that the potential difference between cadmium and alcoholic solutions of some of its salts is not in accord with the theory of Nernst. The present paper is the second of a series which we hope to publish from time to time as the investigation of the electromotive behavior of the metals in nonaqueous solutions progresses. In it an account is given of our studies on the potential differences between zinc and alcoholic solutions of zinc chloride.

Very little work has been done on potentials of zinc in the alcohols. Kahlenberg² measured the potential difference between zinc and zinc chloride in the following combinations:

(A)	(B)	E. M. F. E. M. F. of (A)
$\text{Zn}-0.05 \text{ N ZnCl}_2$ in water. normal electrode		1.082 0.522
$\text{Zn}-0.05 \text{ N ZnCl}_2$ in ethyl alc. normal electrode		0.910 0.350
$\text{Zn}-0.05 \text{ N ZnCl}_2$ in ethyl alc. 0.05 N ZnCl_2 in water—Zn		0.195 0.327

Jones and Smith³ determined the electromotive force of the element

$\text{Zn}-0.1 \text{ N ZnCl}_2$ in ethyl alcohol. . . 0.1 N ZnCl_2 in water—Zn and found it to be 0.195 volt.

No data for the electrical conductivity of zinc chloride in methyl and ethyl alcohols being available, it was necessary to determine this before proceeding to the study of the electromotive behavior of the metal in these solutions.

¹ Getman: *THIS JOURNAL*, **46**, 117 (1911).

² Kahlenberg: *J. Physic. Chem.*, **3**, 379 (1899).

³ Jones and Smith: *THIS JOURNAL*, **23**, 377 (1900).

Electrical Conductivity

Materials Used.—The methyl and ethyl alcohols were obtained from Kahlbaum and were dehydrated for several weeks over lime, after which they were distilled into dry glass-stoppered receivers, the first runnings being discarded. The zinc chloride was obtained from Eimer and Amend and was guaranteed to be pure. It was rendered anhydrous by distilling it in a hard glass tube in a current of dry hydrochloric acid gas, after which the distilled product was immediately transferred to a glass-stoppered weighing bottle and placed in a desiccator over phosphorus pentoxide.

The solutions were made up by direct weighing, the alcohol being freshly distilled and the zinc chloride freshly prepared for each mother solution. Dilutions were made by means of a carefully calibrated burette. Where aqueous solutions were employed, water distilled according to the method of Jones and Mackay was used in making the solutions.

Conductivity Apparatus.—The measurements of electrical conductivity were made by means of Köhler's improved Kohlrausch apparatus. The bridge wire was calibrated by the well known method of Strouhal and Barus. The conductivity cells were of the Arrhenius form, closed by tight-fitting ebonite covers. The constants of these cells were determined by means of 0.02 N potassium chloride, the specific conductivity of which was taken to be 0.002773 reciprocal ohm at 25°. The cell constants were redetermined at frequent intervals. The electrodes of the cells were platinized in the usual manner, it having been demonstrated that the finely divided platinum exerted no appreciable catalytic action during the time of measurement. The electrodes were removed immediately after each measurement to avoid any possible oxidation of the alcohol. The thermostat used to maintain a temperature of 25° was electrically controlled, the maximum temperature variation being about ± 0.05 . By means of a bath of melting ice an average temperature of 0°.2 was maintained for conductivity measurements in the neighborhood of 0°. All thermometers used throughout the investigation were calibrated by comparison with a Reichsanstalt standard ther-

mometer. The solutions were allowed to remain in the baths until the conductivity became constant; this required from twenty to thirty minutes.

Results.—In Table I are given the conductivity data for zinc

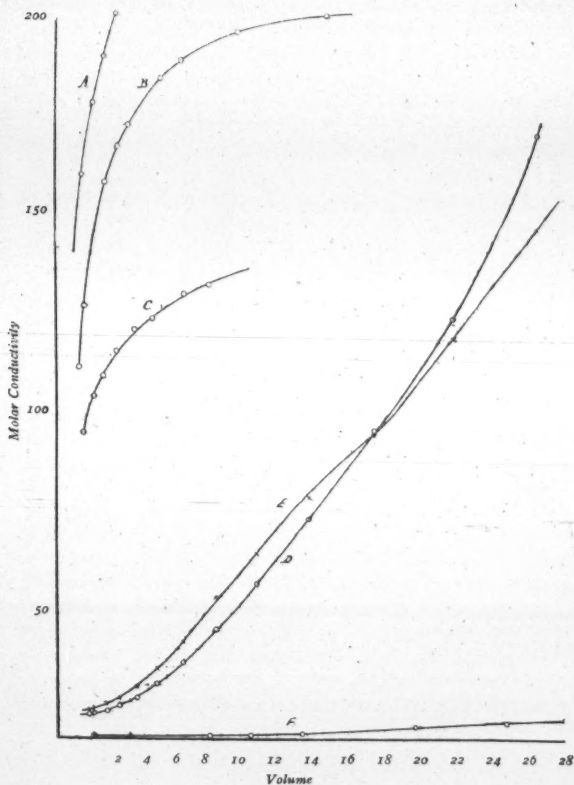


Fig. I

chloride in aqueous solution: m denotes the molar concentration, V is the volume of solution containing one mole, μ_{25° and μ_{0° are the molar conductivities at 25° and 0° , respectively, and β is the temperature coefficient of conductivity. The solutions were diluted by means of two 20 cc. pipettes, one of which was calibrated for capacity and the other for delivery. Dilution was continued until the hydrolysis of the zinc chloride became apparent. The data of Table I are plotted in Fig. I, A and C being the curves for 25° and 0° . The curve marked B was obtained from the work of Kohlrausch¹ on aqueous solutions of zinc chloride at 18° .

Table I.—Zinc Chloride in Water

m	V	μ_{25°	μ_{0°	β
0.2149	4.6533	156.59	85.52	2.84
0.1074	9.3060	176.53	95.136	3.26
0.0537	18.612	189.27	101.15	3.52
0.0269	37.224	201.34	107.58	4.15
0.0134	74.448	213.80	113.16	4.02
0.0067	148.896	221.04	116.44	4.18
0.0034	297.792	227.20	123.47	4.15
0.0017	595.584	238.28	125.95	4.49

The conductivity measurements for the methyl alcohol solutions are recorded in Table II. It will be noticed that with the exception of the most dilute solutions the molar conductivities at 0° are greater than those at 25° , or, in other words, the solutions have negative temperature coefficients. This phenomenon has been observed by Cattaneo² for solutions of hydrochloric acid in ether.

To assure ourselves that this abnormal result was not due to the presence of moisture or to some error in the measurements, the experimental work was repeated from the beginning. A fresh portion of methyl alcohol was distilled and a new sample of zinc chloride was prepared, extra precautions being taken to exclude moisture. The values obtained in the second series of measurements agreed within the limits of experimental error with those of the first.

¹ Kohlrausch: Wied. Ann., **26**, 161 (1885).

² Cattaneo: Rend. r. accad. Lincei, [5] **2**, 295.

The results recorded in Table II are plotted as curves *D* and *E* in Fig. I.

Table II.—Zinc Chloride in Methyl Alcohol

m	V	μ_{25°	μ_{0°	β
0.1982	5.0948	6.8098	7.9034	-0.0437
0.0991	10.1897	6.9437	8.3638	-0.0568
0.0496	20.3793	7.6590	9.5329	-0.0749
0.0248	40.7586	8.9748	11.3102	-0.0934
0.0124	81.5172	11.282	14.346	-0.1225
0.00620	163.034	15.108	19.508	-0.1760
0.00310	326.069	21.131	27.208	-0.2431
0.00155	652.138	30.562	37.815	-0.2901
0.000775	1304.275	42.105	51.65	-0.3418
0.000387	2608.550	61.351	67.511	-0.2464
0.000194	5217.101	85.718	84.720	+0.0399
0.000097	10434.202	116.800	104.180	+0.5048
0.000048	20868.403	173.95	141.056	+1.3157

As will be seen, the curves differ decidedly from those obtained with aqueous solutions. As the dilution increases the curve for 25° crosses the curve for 0° and beyond this point they show a tendency to assume the form *A*, *B* and *C*. This abnormality in the conductivity curves is ascribed to association of the zinc chloride in solution, this phenomenon having been observed by Jones and his coworkers¹ and by one of us in connection with our work on solutions of cadmium iodide in methyl and ethyl alcohols.² That zinc chloride is associated in alcoholic solutions is shown by subsequent determinations of its molecular weight in methyl and ethyl alcohols.

From the fact that the molecular conductivities of the more concentrated solutions in methyl alcohol at 0° are smaller than the molecular conductivities at 25° we infer that the complex formed at the lower temperature is not identical with the complex in solution at the higher temperature.

The results obtained with ethyl alcohol solutions are recorded in Table III:

¹ Jones: *Z. physik. Chem.*, **62**, 41 (1908). Kreider and Jones: *THIS JOURNAL*, **45**, 282 (1911).

² Getman: *Loc. cit.*

Table III.—Zinc Chloride in Ethyl Alcohol

m	V	μ_{25°	μ_{40°	β
0.1316	7.5979	0.3219	0.2018	0.0048
0.0658	15.1957	0.3242	0.1990	0.0050
0.0329	30.3914	0.3255	0.2119	0.0045
0.0263	37.9893	0.3013	0.1995	0.0041
0.0165	60.7829	0.3236	0.2136	0.0044
0.0132	75.9786	0.3384	0.2197	0.0048
0.00823	121.5658	0.3773	0.2439	0.0053
0.00628	151.9572	0.3947	0.2619	0.0053
0.00411	243.1315	0.4968	0.3150	0.0073
0.00329	302.9144	0.5296	0.3435	0.0074
0.00206	486.2630	0.5606	0.3685	0.0077
0.00165	605.8288	0.7207	0.4593	0.0105
0.000823	1211.6576	1.0756	0.6538	0.0169
0.000411	2423.3152	1.5209	1.0495	0.0189
0.000263	3798.967	2.4311	1.5959	0.0334
0.000206	4846.630	2.2922	1.7165	0.0232
0.000132	7597.934	3.5986	2.5483	0.0420
0.000066	15195.868	4.4225	2.9892	0.0573

The vertical scale of Fig. I being too small to admit of representing the conductivity in ethyl alcohol at 0° and 25° , the data for the higher temperature alone are plotted at F , while in Fig. II the data for the two temperatures are plotted on a larger vertical scale.

Here the conductivities at 0° lie below those at 25° , but the form of the curves is much the same as with methyl alcohol. Again we attribute this departure from the normal conductivity curve to association of the solute.

Molecular Weight Determinations.—In order to confirm the supposition that zinc chloride is associated in the alcoholic solutions molecular weight determinations were made by means of the boiling point method. The results are given in Table IV:

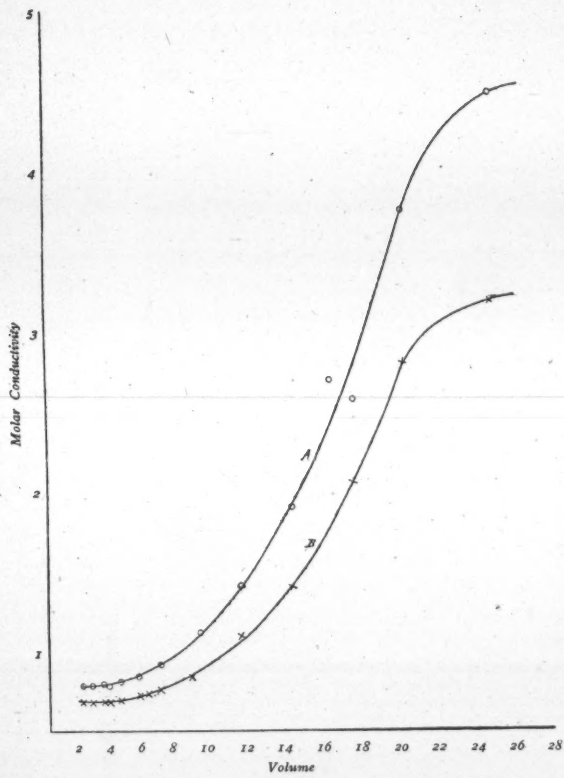


Fig. II

Table IV.—Molecular Weight of Zinc Chloride

Solvent: CH_3OH		Solvent: $\text{C}_2\text{H}_5\text{OH}$	
Molar concentration	Molecular weight	Molar concentration	Molecular weight
0.2	190.7	0.214	149.4
0.2	198.2	0.214	155.8
0.2	187.2	0.107	146.9
0.2	200.8	0.107	148.9
Mean,	194.2	Mean,	150.2

The molecular weight of zinc chloride as calculated from the formula is 136.43. The above results show that the solute is associated in both solvents, the association in methyl alcohol being greater than in ethyl alcohol.

Electrode Potentials

Apparatus.—The apparatus used in this investigation was similar to that employed in our previous work on cadmium in alcoholic solutions with the exception of the electrode vessels, a sketch of which is given in Fig. III. The vessel A contained

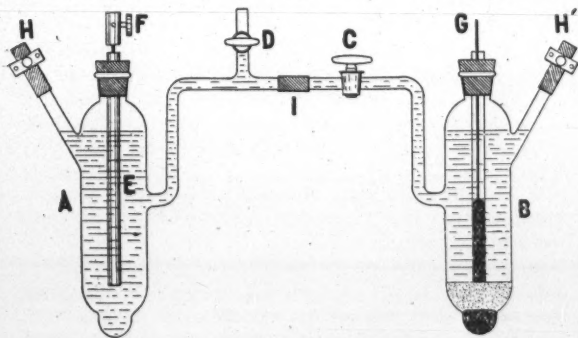


Fig. III

the solution and the zinc electrode E. By means of the side tube and rubber tube, I, connection was established with the other vessel, B, which served as the calomel electrode. The

connecting tube was filled with solution by opening the stopcocks C and D and blowing gently through a glass tube inserted in the rubber tubing at H', the screw pinchcock at this point being opened. The pressure of the air forces some of the N potassium chloride solution from the calomel electrode through C and I, any air bubbles escaping at D. The stopcocks were now closed, as was also the pinchcock H', and the experimental cell was introduced into the circuit by means of the connections F and G.

The zinc electrode, E, was made by casting Baker & Adamson's purest zinc in the form of a cylindrical rod 5 mm. in diameter and 8 cm. long, after which a stout copper wire and connector was soldered to one end.

The surface of the zinc was cleaned by immersion in dilute acid and subsequent washing in distilled water. Before inserting the electrode in the solution, the surface was thoroughly amalgamated.

Two cells were employed, one being placed in the 25° bath while the other was maintained at 0°, as in the measurement of the electrical conductivity of the solutions.

After the cells had acquired the temperature of the bath the stopcock C was opened just long enough to determine the point of balance on the bridge wire. By keeping C closed except when making measurements, diffusion is minimized. As in our previous work, we have assumed that any electromotive force which may be set up at the junction of the solutions is negligible.

Results.—The electrode potentials in aqueous solutions were found to follow Nernst's law provided the concentration was above 0.1 molar.

In less concentrated solutions the electrode potential becomes steadily smaller, instead of increasing (i. e., becoming more negative) as Nernst's law requires. This anomalous behavior in dilute solutions led us to repeat these determinations with great care, with the result that in the second series of measurements the potentials were again too small but widely divergent from the values obtained in the first series for the same concentrations. The electrode potentials were found to

vary with time, but the variation was so erratic as to preclude any explanation based upon progressive changes in the solutions or on the electrodes. In a paper on the electrometric method for the determination of hydrolysis, Denham¹ encountered similar difficulties with aqueous solutions of zinc chloride and states that the potential fluctuated most erratically over a period of four weeks, when further measurements were abandoned. As a result of his observations he suggests that the phenomenon may be due to the formation of colloidal substances which interfere with the normal course of hydrolysis.

The observed values of the electrode potentials at 0° and 25° are given in Table V, together with the values of the potentials calculated by means of the equation

$$\pi_1 = \pi_0 + \frac{RT}{nF} \log_e \frac{m_1 \mu_1}{m_0 \mu_0}$$

where π_1 and π_0 are the electrode potentials corresponding to solutions of molar concentrations m_1 and m_0 , and molar conductivities μ_1 and μ_0 . The symbols R , T , F and n have their usual significance. The electrode potential in the most concentrated solution is taken as π_0 in calculating the other potentials.

Table V.—Zinc Chloride in Water

m	μ_{25}	μ_0	π_{25}° (obs.)	π_{25}° (calc.)	π_0° (obs.)	π_0° (calc.)
0.3010	155.0	84.5	-0.509	-0.509	-0.525	-0.525
0.21488	156.6	85.5	-0.511	-0.513	-0.526	-0.529
0.16116	168.0	91.0	-0.514	-0.515	-0.527	-0.532
0.10744	176.5	95.1	-0.518	-0.520	-0.527	-0.536

The data of Table V are plotted in Fig. IV. Logarithms of $m\mu$, being proportional to the ionic concentrations, are chosen as abscissas and electrode potentials as ordinates. A and B represent electrode potentials as a function of ionic concentration at 25° and 0°, while C represents the results of Labendzinski² on the electrode potentials of zinc in aqueous zinc chloride solutions, presumably at 25°, although this author does not mention the temperature at which he worked. It

¹ Denham: J. Chem. Soc., 93, 41 (1908).

² Labendzinski: Z. Elektrochem., 10, 77 (1904).

will be observed that in every case the calculated potentials are slightly greater than the experimental values.

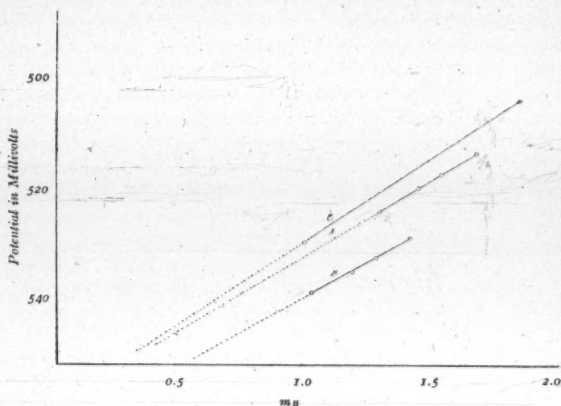


Fig. IV

The individual measurements are accurate to within two millivolts, so that where the difference between the observed and calculated potentials exceeds this value, the error must be ascribed to some source other than the method employed in making the measurements.

The dotted portions of the curves A, B and C may be used to obtain by extrapolation the values of the electrode potentials in the more dilute solutions where the experimental data are untrustworthy.

From the data of Table V it is possible to calculate the heat of ionization of zinc by means of the equation of Helmholtz,

$$\pi = \frac{Q}{nF} + T \frac{d\pi}{dT}$$

where π is the electrode potential of zinc in a molar solution of zinc ions, Q is the heat produced when one gram equivalent of zinc passes from the metallic to the ionic state, and F , T

and n have their usual significance. Rearranging the equation, we have:

$$Q = \left(\pi - T \frac{d\pi}{dT} \right) nF$$

To determine the value of π , we make use of the Nernst equation,

$$\pi_1 = \pi_0 + 0.0295 \log \frac{m_1 \mu_1}{m_0 \mu_0}$$

Taking $\pi_0 = -0.509$ volt and $\mu_1 = 115$ (conductivity of molar zinc chloride at 25°),

$$\pi_1 = -0.509 + 0.0295 \log \frac{115}{0.301 \times 155}$$

$$\pi_1 = -0.497 \text{ volt}$$

Substituting this value in the Helmholtz equation, we have

$$Q = (-0.497 - 298 \times 0.000664)(2 \times 96540 \times 0.2394) = 32120 \text{ cal.}$$

This value compares well with the following results obtained by Ostwald¹ and Jahn:²

	Ostwald	Jahn	G. and G.	Mean
Heat of ionization of zinc (calc.)	32600	33950	32120	32890

The data for zinc chloride in methyl alcohol solutions are given in the following table:

Table VI.—Zinc Chloride in Methyl Alcohol

m	π_{25°	π_{0°	m	π_{25°	π_{0°
0.2000	-0.366	-0.382	0.0542	-0.402	-0.410
0.1750	-0.409	-0.424	0.0257	-0.410	-0.426
0.1500	-0.434	-0.447	0.0103	-0.430	-0.451
0.1250	-0.393	-0.418	0.0021	-0.409	-0.426
0.1029	-0.415	-0.418	0.0001	-0.419	-0.447
0.0750	-0.434	-0.460			

An inspection of this table will show that the electrode potentials fluctuated over a range of more than a centivolt, a variation much larger than the experimental error. This

¹ Ostwald: *Z. physik. Chem.*, **11**, 501 (1893).

² Jahn: *Ibid.*, **18**, 399 (1895).

somewhat anomalous behavior of zinc in methyl alcohol solutions of zinc chloride is being studied in this laboratory at the present time and will be made the subject of a future paper.

The change in potential of the zinc electrode in solutions of zinc chloride in ethyl alcohol is very uniform, as will be seen from Table VII and Fig. V, curve A representing the potentials at 25° and Curve B those at 0°:

Table VII.—Zinc Chloride in Ethyl Alcohol

<i>m</i>	π_{25°	π_{0°	<i>m</i>	π_{25°	π_{0°
0.2138	—0.399	—0.407	0.0535	—0.352	—0.388
0.1604	—0.383	—0.398	0.0268	—0.340	—0.385
0.1069	—0.366	—0.396	0.0134	—0.337	—0.378
0.0800	—0.354	—0.388			



Fig. V

The abnormality of the conductivity curves for solutions of zinc chloride in ethyl alcohol (Fig. II) renders uncertain any calculation of the degree of ionization of the solute, hence in representing graphically the data of the foregoing table we have plotted molar concentrations as abscissas instead of attempting to plot ionic concentrations as in Fig. IV. The electrode potential is nearly a linear function of the molar concen-

tration, the slope of the line being dependent upon the temperature. If this linear relation holds for solutions of greater concentration than those with which we have worked a reversal of temperature coefficients must occur, solutions of concentration above 0.24 molar having positive instead of negative coefficients.

The value of the electrode potential diminishes with dilution instead of increasing as in aqueous solutions. This is in agreement with the results obtained by one of us¹ in our investigation of the behavior of the cadmium electrode in alcoholic solutions of cadmium salts. A comparison of our results with those of Kahlenberg² for solutions of approximately the same concentration is of interest as a check on the accuracy of the measurements. He found for a 0.05 molar solution of zinc chloride in ethyl alcohol at room temperature an electrode potential of -0.350 volt while we obtain for a 0.0535 molar solution at 25° a potential of -0.352 volt, the agreement being most satisfactory.

In view of the abnormal conductivities of solutions of zinc chloride in ethyl alcohol and the inverse variation of electrode potential with concentration in these solutions, it is obvious that any attempt to calculate the solution pressure of zinc in ethyl alcohol would be futile.

SUMMARY

(1) The electrical conductivities of solutions of zinc chloride in water, methyl alcohol and ethyl alcohol have been measured. The conductivities in aqueous solutions are normal while those in alcoholic solutions give evidence of association of the solute and also of possible complex formation between solute and solvent. The more concentrated solutions in methyl alcohol have negative temperature coefficients.

(2) Molecular weight determinations by the boiling point method have shown that in both alcohols zinc chloride is associated, the association in methyl alcohol being greater than in ethyl alcohol.

(3) The potentials of zinc in aqueous and alcoholic solu-

¹ Getman: *Loc. cit.*

² Kahlenberg: *Loc. cit.*

tions of zinc chloride have been determined by measuring the electromotive force of the combination

Zn-Sol. ZnCl_2 —Calomel Electrode

and deducting $0.56 + 0.0006t$, the potential of the calomel electrode. The electrode potential of zinc in aqueous solutions has been shown to follow Nernst's law in the more concentrated solutions, but in the dilute solutions the experimentally determined potentials are much smaller than the calculated.

The potentials in methyl alcohol solutions oscillate over a range of more than ten millivolts. This variation is being made the subject of a special investigation.

Zinc in ethyl alcohol solutions gives with decreasing concentration a uniformly diminishing potential, this behavior being the reverse of that in aqueous solutions.

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A STUDY OF THE REFRACTIVE INDICES OF SOLUTIONS OF THE CADMIUM HALIDES

BY FREDERICK H. GETMAN AND HELEN T. GILROY

The refractive indices of solutions of the halides of cadmium have been measured by several investigators.¹ After reviewing the work of these experimenters and having noted some lack of agreement between the results it seemed desirable to redetermine with great care the refractive indices and densities of solutions of cadmium chloride, cadmium bromide and cadmium iodide.

Materials Used.—The salts used in this investigation were prepared by the Hoffmann & Kropff Chemical Company, and were guaranteed to be pure. The solutions were made up with conductivity water having a mean specific conductivity of 1.5×10^{-6} reciprocal ohms. The salts were dehydrated by prolonged confinement in a desiccator over concentrated sulphuric acid and subsequent heating to con-

¹ Bender: Wied. Ann., **39**, 89 (1890). Barbier and LeRoux: Compt. rend., **110**, 458 (1890). Jahn: Wied. Ann., **43**, 280 (1891). De Muynck: *Ibid.*, **53**, 561 (1894). Gladstone and Hibbert: J. Chem. Soc., **67**, 831 (1895). Le Blanc and Rohland: Z. physik. Chem., **19**, 282 (1896). Hallwachs: Wied. Ann., **68**, 30 (1899).

stant weight. The solutions were prepared by direct weighing of both salt and solvent, the concentrations being expressed in per cent. of salt.

Apparatus and Method.—The densities of the solutions were determined in a Sprengel-Ostwald pyknometer of approximately 6 cc. capacity. The pyknometer was suspended in a thermostat maintained at $25^{\circ} (\pm 0.1)$ for about fifteen minutes, after which its contents were adjusted so that the meniscus was tangent to the mark on the stem. The densities were calculated by the familiar formula

$$d_4^{25} = \frac{W_1}{W_2} (Q - \lambda) + \lambda$$

where

d_4^{25} = density of solution at 25° referred to water at 4°

W_1 = weight of solution

W_2 = weight of an equal volume of water

Q = density of water at $25^{\circ} = 0.99707$

and

λ = mean density of air = 0.0012

The refractive indices were measured with the improved form of Pulfrich refractometer manufactured by Zeiss and furnished with a Van Aubel thermostat. The temperature of the solution and prism could be maintained at $25^{\circ} (\pm 0.1)$ for several hours, thus minimizing an error which has been more or less indeterminate in some of the earlier investigations on refractive indices. The refractive index of each solution has been measured for the *D* line of sodium and for the *C* and *F* lines of hydrogen.

Before proceeding to make any measurements with the refractometer the error of the zero reading of the instrument was determined and all subsequent readings were corrected. In addition to the correction of the zero of the instrument correction for the temperature of the prism was applied, these two corrections insuring an accuracy in the refractive indices of two units in the fifth place of decimals.

Before entering upon the study of the solutions the refractive index of the water used as a solvent was determined with great care. The mean of several determinations of the refractive index for the *D* line was 1.33250, which agrees very

well with the value, 1.33248, recently found by Baxter, Burgess and Daudt¹ as the result of a special investigation of the refractive index of water.

To insure the solutions having acquired the temperature of the thermostat and to prevent changes in concentration due to evaporation of the solvent, the cell of the refractometer was closed by means of the tight-fitting rim of the heating vessel and the solution allowed to stand for thirty minutes before taking any readings.

Results.—The formula of Lorentz² and Lorenz³ was used in calculating the specific refractions of the solutions, it being generally conceded that the values obtained by the use of this formula are more nearly constant under varying conditions than the values given by the Gladstone and Dale or other empirical relations.

As Baxter and his coworkers⁴ have pointed out, none of the formulas for specific refraction are entirely satisfactory and consequently any relationship which is dependent upon specific refraction is more or less uncertain.

We have assumed that the specific refractions of solute and solvent are additive and have calculated the specific refraction of the salt from the specific refractions of the solution and water according to the formula

$$r = \frac{1}{p} \left(\frac{n^2 - 1}{n^2 + 2} \cdot \frac{100}{d} - \frac{n_w^2 - 1}{n_w^2 + 2} \cdot \frac{100 - p}{d_w} \right)$$

where r = specific refraction of salt in solution

p = per cent. of salt

n = index of refraction of solution at 25°

n_w = index of refraction of solvent at 25°

d = density of solution at 25°

and d_w = density of water at 25°

In the tables which follow p , d and r have the same significance as above, while n_C , n_D and n_F denote the indices of refraction for the C, D, and F lines and M is the molecular weight of the solute.

¹ Baxter, Burgess and Daudt: J. Am. Chem. Soc., **33**, 893 (1911).

² Lorentz: Wied. Ann., **9**, 642 (1880).

³ Lorenz: *Ibid.*, **11**, 70 (1880).

⁴ Baxter, Boylston, Mueller, Black and Goode: J. Am. Chem. Soc., **33**, 901 (1911).

Table I.—Cadmium Chloride in Water (25°)

p	d	n_D	n_F	$\frac{n_D^2-1}{n_D^2+1} \cdot \frac{1}{d}$	r	M_r
1.599	1.0115	1.33325	1.33517	0.2045	0.1063	19.48
4.472	1.0368	1.33755	1.33929	0.2018	0.1118	20.48
8.620	1.0695	1.34292	1.34499	0.1985	0.1195	21.91
11.600	1.1068	1.34858	1.35088	0.1948	0.1086	19.91
18.690	1.1803	1.36110	1.36316	0.1885	0.1124	20.60
21.201	1.2165	1.36615	1.36833	0.1851	0.1071	19.63
26.076	1.2700	1.37631	1.37850	0.1818	0.1127	20.60
31.090	1.3401	1.38681	1.38925	0.1756	0.1081	19.82
41.540	1.5153	1.41436	1.41710	0.1662	0.1103	20.21

Mean, 20.30

Table II.—Cadmium Bromide in Water (25°)

p	d	n_D	n_F	$\frac{n_D^2-1}{n_D^2+1} \cdot \frac{1}{d}$	r	M_r
1.05	1.0059	1.33043	1.33330	0.2049	0.1047	28.49
2.76	1.0212	1.33430	1.33623	0.2032	0.1015	27.63
5.41	1.0470	1.33834	1.34001	0.2002	0.0980	26.68
11.03	1.1016	1.34599	1.34782	0.1902	0.1047	28.49
15.66	1.1509	1.35308	1.35500	0.1893	0.0990	26.95
21.13	1.2133	1.36213	1.36425	0.1840	0.1017	27.68
27.51	1.2991	1.37381	1.37624	0.1767	0.0996	27.11
40.74	1.4918	1.40130	1.40373	0.1639	0.1026	27.93

Mean, 27.62

Table III.—Cadmium Iodide in Water (25°)

P	d	n_D	n_F	$\frac{n_D^2 - 1}{n_D^2 + 2} \cdot \frac{1}{d}$	r	Mr
0.834	1.0042	1.33186	1.33804	0.2052	0.1079	39.52
3.340	1.0249	1.33548	1.34151	0.2030	0.1108	40.56
3.880	1.0303	1.33547	1.34193	0.2023	0.1109	40.60
6.984	1.0581	1.34021	1.34699	0.1993	0.1103	40.38
13.491	1.1216	1.35049	1.35706	0.1932	0.1112	40.71
20.133	1.1933	1.36167	1.36435	0.1869	0.1113	40.75
26.785	1.2780	1.37553	1.38508	0.1805	0.1105	40.46
39.860	1.4801	1.40798	1.41952	0.1678	0.1101	40.32
					Mean,	40.41

Summary of Results

It will be observed on inspection of the foregoing tables that the specific and, consequently, the molecular refractions are nearly constant over the entire range of concentrations, the slight variations in the specific refractions being greatly magnified when these are multiplied by the molecular weights of the respective salts. It seems justifiable to select the mean of the molecular refractions of the solutions of each salt as a close approximation to its true molecular refraction.

In their paper on the refractive indices of aqueous solutions of the halogen salts of lithium, sodium and potassium, Baxter and his students¹ have computed the atomic refractions of the constituents of the salts studied, assuming the value of the atomic refraction of hydrogen to be 1.03.

The following table gives the mean values of the atomic refractions as calculated by Baxter:

Table IV

Hydrogen	1.03	Lithium	1.27
Chlorine	7.50	Sodium	1.75
Bromine	11.05	Potassium	3.24
Iodine	17.68		

Taking the values for the atomic refractions of chlorine, bromine and iodine as here given, we may calculate the atomic refraction of cadmium from the mean values of the molecular refractions of its halogen salts, thus:

$$\begin{aligned}
 20.30 \text{ (mol. ref. CdCl}_2\text{)} - 15 (2 \times \text{at. ref. Cl}) &= 5.30 \text{ at. ref. Cd} \\
 27.62 \text{ (mol. ref. CdBr}_2\text{)} - 22.1 (2 \times \text{at. ref. Br}) &= 5.52 \text{ at. ref. Cd} \\
 40.41 \text{ (mol. ref. CdI}_2\text{)} - 35.36 (2 \times \text{at. ref. I}) &= 5.05 \text{ at. ref. Cd}
 \end{aligned}$$

$$\text{Mean, } \underline{\underline{5.29}}$$

While it would be unwise to attempt to formulate any generalization from such a limited amount of data it is of interest to review very briefly some of the facts which must be considered when such a generalization is established.

Gladstone² has shown that the product of the specific re-

¹ *Loc. cit.*

² Gladstone: P. Roy. Soc., **60**, 140 (1896).

fraction and the square root of the equivalent weight of an element is a constant the value of which for univalent metals is approximately 1.30 and for polyvalent metals about 1.01, these values being computed from specific refractions derived by means of the Gladstone and Dale formula. This relation between valence and specific refraction suggests a connection between refraction and volume, it having been pointed out by Traube,¹ LeBas,² and Barlow and Pope³ that there exists a simple relationship between valence and volume. Further evidence of the existence of some relation between refraction and volume has been furnished by Traube,⁴ who has shown that b , the volume factor in van der Waals' equation, is about 3.5 times as large as the molecular refraction calculated by means of the Lorentz-Lorenz formula. Exner⁵ has pointed out that the molecular refraction of a compound calculated by means of the Lorentz-Lorenz formula is nearly proportional to the volume occupied by the atoms. On the assumption that molecular refraction is a measure of the nuclear volumes of the atoms in a substance, Traube has shown that in a series of carbon compounds of various classes the ratio of the molecular refraction to the total number of valences of the constituent atoms is a constant. This constant he terms the refraction stere.

If the sum of the external volumes of the atoms is represented by b in van der Waals' equation and the nuclear volume is represented by Mr then $b-Mr$ must be a measure of the atomic volumes and the ratio of $b-Mr$ to n , the total number of valences, will represent what Traube calls the valon stere. Traube defines a valon as an active group of electrons occupying the covolume, the active electrons endowing the atom with valence. The valon steres for a series of hydrocarbons, amines and esters are found to approximate to a constant value.

All of the above relations fail to apply to the halides of lithium, sodium, potassium and cadmium, but since these

¹ Traube: *Ber. d. chem. Ges.*, **40**, 130, 723, 734 (1907).

² Le Bas: *J. Chem. Soc.*, **91**, 112 (1907).

³ Barlow and Pope: *Ibid.*, **89**, 1675 (1906); **91**, 1150 (1907).

⁴ Traube: *Drude's Ann.*, **5**, 552 (1901).

⁵ Exner: *Wien. Ber.*, **91**, 85 (1885).

substances are so different in chemical character from those studied by Traube it could hardly be expected that the same relationships would be found to apply, at least without some modification.

Richards¹ has shown that there is a close relationship between the atomic volumes of the elements and their compressibilities. If the compressibilities of the elements are plotted against their atomic weights the curve obtained indicates that one is a periodic function of the other.

Hauke² has studied the relation between the specific refractions and the atomic weights of the elements and he finds it to be periodic, the specific refraction increasing to a maximum at the middle of each period and diminishing towards the end.

In the following table are given the values of the atomic volumes, the atomic refractions and the compressibilities of the elements mentioned above:

Table V

Element	At. vol.	At. refr.	Comp.
Lithium	13.1	1.27	8.8
Sodium	23.7	1.75	15.4
Potassium	45.5	3.84	31.5
Cadmium	13.0	5.29	1.9

While there is no self-evident mathematical relation connecting these various magnitudes yet there is evidently some underlying principle which, when discovered, will make possible the expression of atomic refraction in terms of such quantities as atomic volume, compressibility and valence.

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A STUDY OF THE CHANGE FROM VIOLET TO GREEN IN SOLUTIONS OF CHROMIUM SULPHATE

BY MINNIE A. GRAHAM

INTRODUCTION

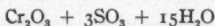
In 1841 Schrötter,³ while studying a series of compounds

¹ Richards: *Z. Elektrochem.*, **13**, 519 (1907).

² Hauke: *Wien. Ber.*, **105**, IIA, 749 (1896).

³ *Pogg. Ann.*, **63**, 513 (1841).

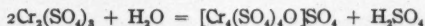
formed by sulphuric acid and chromic oxide, observed the existence of one of the products in two varieties. From a solution of anhydrous chromic sulphate in sulphuric acid, he obtained, by precipitation with alcohol, a light violet, crystalline salt, which resembled chrome alum. In accordance with his analytical results, he represented this salt by the formula



The green filtrate from the violet salt, on evaporation, left a green amorphous substance which he regarded as another form of chromic sulphate. He concluded that there were two modifications of the solution of neutral chromic sulphate, from one of which he had obtained the violet salt and from the other the green substance.

Schrötter also observed that a solution of the violet compound became green when heated to 70° , and attributed this change in color to loss of water. Krüger¹ afterwards observed the same change and proved that the green solution contained free acid.

Since the time of Schrötter and Krüger this interesting phenomenon has been a favorite subject of investigation. Favre and Valson² showed that only a fraction of the sulphate ion in the green solution is precipitated by barium chloride, and they assumed that the remainder forms a complex with the chromium. Recoura,³ on the other hand, decided that the green solution contains free acid and a sulphate formed in accordance with the equation



and that the precipitated barium sulphate obtained by Favre and Valson was derived in part from the salt and in part from the free acid. From results obtained by thermochemical measurements, Recoura concluded that one molecule of free acid is present in the green solution of two molecules of chromic sulphate.

¹ Pogg. Ann., **61**, 218 (1843).

² Compt. rend., **74**, 1016 (1872).

³ Ann. chim. phys., [7] **4**, 494 (1895).

Whitney,¹ in 1896, found that the electrical conductivity of the green solution is much greater than that of the violet solution of the same concentration, and attributed this difference to the presence of free acid in the green solution. He found also that addition of alkali to the green solution at first decreases the conductivity and that this decrease ceases when one molecule of sodium hydroxide has been added for each molecule of chromium sulphate in the original solution, further addition of the base increasing the conductivity. This diminution in conductivity is evidently due to neutralization of free acid by the base. This is in agreement with the conclusion of Recoura² previously referred to. The conductivity of the violet solution is only slightly diminished and soon begins to increase when sodium hydroxide is added. Whitney³ later confirmed the presence of free acid in the green solutions by means of experiments on the velocity of ionic migration.

In 1903 Richards and Bonnet⁴ undertook the determination of the amount of free acid in the solutions by measuring the extent of the inversion produced in solutions of cane sugar by solutions of chromium sulphate. They also carried out experiments in dialysis and neutralization which indicated the presence of free acid in the solutions, and by measurements of ionic migration they showed that there is present no anion containing chromium and, therefore, no ionized complex acid such as $\text{HCr}(\text{SO}_4)_2$, which some investigators have assumed to be formed.

Denham,⁵ a few years later, made a careful study of the degree of hydrolysis in both solutions by means of measurements of the potential of cells made up in the following form:

- I. H_2 —violet solution—calomel electrode, and
- II. H_2 —green solution—calomel electrode

He concluded that the hydrolysis of the normal violet chromium sulphate is somewhat greater than that of alumin-

¹ *Z. physik. Chem.*, **20**, 40 (1896).

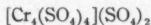
² *Loc. cit.*

³ *J. Am. Chem. Soc.*, **21**, 1078 (1899).

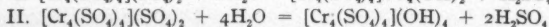
⁴ *Z. physik. Chem.*, **47**, 29 (1904).

⁵ *Z. anorg. Chem.*, **57**, 361 (1908).

ium sulphate; that the green salt contains a complex cation and may be represented by the formula



that this salt is strongly hydrolyzed in solution according to the equations:



Equation I represents concentrated solutions and Equation II dilute solutions.

It will be seen from this brief historical survey that the problem under investigation has been attacked in a variety of ways and with different objects in view. The principal physico-chemical methods that have been applied, heretofore, are those used in the measurement of dialysis, electrical conductivity, potential, catalytic inversion of sugar, depression of the freezing point and ionic migration. In the present investigation, the purpose has been to study more closely the conditions under which the color change takes place and the variation in the properties of the solutions that accompany this change of color, and, also, to determine, if possible, the degree of hydrolysis in the two solutions.

With this end in view, I measured the density, viscosity and electrical conductivity of both the violet and green solutions, studied the catalytic effect of these solutions on the inversion of sugar, and photographed the absorption spectra of both solutions through a wide range of concentrations.

The Preparation of Violet Chromium Sulphate

For the purpose of the research, it was necessary to prepare a sufficient supply of pure chromium sulphate in its violet modification. The method of Traube,¹ as modified by Richards and Bonnet,² seemed more satisfactory than others and was accordingly followed. This consists in the reduction, by means of alcohol, of chromic acid in solution in water and sulphuric acid. Richards and Bonnet found that by careful

¹ Ann. Chem. (Liebig), **66**, 88 (1848).

² Loc. cit.

cooling and slow addition of alcohol the yield of violet salt was much increased. Preliminary to the preparation of a larger quantity the work of Richards and Bonnet was followed, using twenty grams of chromic acid and thirty grams of pure sulphuric acid dissolved in sixty grams of water. This preparation required nearly three days and yielded fourteen grams of the violet salt. The quantities of chromic acid, sulphuric acid and water were then increased ten-fold, the resulting solution was cooled to -5° in a freezing mixture and reduced with 95 per cent. alcohol that had been cooled in an ice chest. The alcohol was added very slowly from a dropping funnel while the solution was constantly agitated, the temperature being kept as low as possible—approximately 8° —though occasionally, because of the heat evolved in the reduction, it went a little above 10° . Alcohol was added at intervals until a quantity sufficient for the reduction had been used. Very little solid separated from the solution during the first 24 hours; but when the mixture was allowed to stand out of doors at a temperature of about 5° for 17 hours longer, it deposited a heavy green precipitate. Further addition of cold alcohol to the solution, the beaker being surrounded by a freezing mixture, produced no appreciable rise in temperature, indicating that the reduction was complete. The precipitate, when filtered upon a Buchner funnel and washed with cold alcohol, appeared grayish green by daylight and lavender by electric light. It was dissolved in the smallest possible quantity of pure ice-water, giving a deep blue solution with a tendency to become green at room temperature. To this blue solution cold absolute alcohol was added and a light violet, crystalline precipitate with a pearly luster was obtained, which was filtered, washed sparingly with absolute alcohol, and further purified by solution in ice-water and reprecipitation with absolute alcohol. The final product was not washed, but dried as thoroughly as possible between layers of filter paper, and finally placed in a large desiccator containing sticks of potassium hydroxide. In the moist condition the product shows a tendency to become green at room temperature; but after thorough drying a violet powder, apparently stable in the

air, is obtained. This preparation gave a yield of seventy-seven grams, and required nearly five days for its completion. A year later, when another preparation was necessary, special care was taken to control the conditions so as to increase the yield if possible. As previous results seemed to indicate that time is an important factor in the formation of the salt, the solution was left in an ice chest for intervals of several hours between successive additions of alcohol. The alcohol was added so slowly that the temperature never rose above 10° , and for the greater part of the time it was kept as low as 5° , the solution being cooled to 0° or -3° during the intervals between additions. In the process of purification all solutions were kept as cold as the solubility of the salt permitted, and the desiccator containing the final product was kept in an ice chest. This preparation took ten days and yielded one hundred and seventy grams, the initial solution having been made from two hundred grams of chromic acid, three hundred grams of sulphuric acid and six hundred grams of water. It would be interesting to study more thoroughly the influence of time upon the yield, as it was observed that the cooled filtrates, upon standing, deposited considerable quantities of the violet salt, and it is possible that the yield might be still further increased by allowing more time for deposition.

Analyses

The violet salt was analyzed for chromium by ignition to the oxide.

- I. 1.0738 grams of salt gave 0.2381 gram Cr_2O_3 .
- II. 0.8806 gram of salt gave 0.1958 gram Cr_2O_3 .

	Calculated for $\text{Cr}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$	I	Found	II
Cr_2O_3	22.33	22.17		22.24

The sulphuric acid in the same salt was determined by precipitation with barium chloride, care being taken to avoid occlusion of chromium compounds. Barium sulphate was precipitated from a cold solution of the salt, to which hydrochloric acid had been added, and the mixture was thoroughly boiled before filtration.

- I. 0.5810 gram of salt gave 0.5877 gram BaSO_4 .
 II. 0.6213 gram of salt gave 0.6308 gram BaSO_4 .

	Calculated for $\text{Cr}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$	I Found	II Found (by difference)
SO_3	35.30	34.69	34.86
H_2O	42.36		43.00

For each gram molecule of chromic oxide there were found to be 2.96 gram molecules of sulphuric acid, expressed as sulphur trioxide, indicating that the salt is normal. The water was found by difference to be 43.00 per cent., corresponding to 16.36 H_2O . Varying amounts of water have been assigned to the salt by different investigators. It is probable that the salt loses water when kept in a desiccator, although no change in the appearance of the dried salt has been observed. A specimen dried entirely in the air gave a value of 22.35 per cent. for chromic oxide, while a small quantity dried in a vacuum desiccator gave 23.59 per cent.—the value calculated for $\text{Cr}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$. Other specimens, left for a long time in the potassium hydroxide desiccator, gave values of 23.72 and 23.64 per cent. of chromic oxide, indicating a loss of water after long standing over potassium hydroxide.

Density of Solutions

The first property to be studied quantitatively was the density of solutions. In the preparation of solutions the weight of violet salt calculated for a given concentration was dissolved in pure ice-water in a graduated flask; the solution was allowed to reach room temperature, and then diluted to the mark. The weight of salt was calculated on the basis of the formula $\text{Cr}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$, and the concentration of the chromium was afterwards determined by evaporating a definite volume of the solution and igniting the residue. The solutions exhibit a rich violet color by transmitted light, and a deep blue surface color. Experience has shown that the solutions gradually lose their violet color at room temperature and become greenish blue. Although the amount of hydrolysis at this temperature may not seriously affect the phys-

ico-chemical measurements to be made, it was thought best to keep the solutions in an ice chest.

For the determination of density a Sprengel-Ostwald pycnometer, having a volume of approximately twenty cubic centimeters, was employed for temperatures between 20° and 95°, and a Reischauer specific gravity flask, of about the same volume, with a long graduated neck, for temperatures below 20°. These were calibrated with water for the desired ranges of temperature and a curve plotted for use in the calculation of the density of the solutions at different temperatures. A large beaker served as bath, the pycnometer or flask being suspended in the bath long enough for the temperature of the liquid to become constant, then brought to the temperature of the balance and weighed. A constancy of 0.01 was possible during these determinations. The same method was followed in weighing the chromium solutions: a solution of violet salt was introduced into the pycnometer, kept in the bath for a sufficient length of time to insure constancy of temperature, and then weighed. The temperature of the bath was raised five or ten degrees and the pycnometer again suspended, no change being made in the solution except as it became necessary to add or remove a small quantity in order to adjust the volume to the fixed mark of the pycnometer. As the temperature was raised the blue solution was observed to change gradually in appearance and between 40° and 50° it became decidedly green. The temperature was carried to 90° or 95°, the values calculated from the weights being taken as the density of the violet solution at the different temperatures. The bath was then cooled five or ten degrees at a time, and the pycnometer containing the solution was weighed for successive temperatures as before. The values calculated from these observations are taken as the density of the green solution with varying temperature. It was noticed that above 90° water evaporated from the green solution and so, in general, the determinations were not made beyond this temperature.

The densities were calculated from the usual expression,

$$d_4^{t^o} = \frac{w_t}{w_a} (Q - L) + L$$

where d represents the density of the solution; w_s the apparent weight of the solution in air; w_a the weight of an equal volume of water; Q the specific gravity of water at temperature t ; and $L = 0.0012$, the mean density of air with reference to water at 4° . The values obtained are given in the following tables:

Table I.—Density
0.1024 Molar Solution

Temp.	Violet	d	Temp.	Green	d
0°		1.0394	95°		0.9973
$4^\circ.5$		1.0392	90°		1.0017
10°		1.0391	85°		1.0039
15°		1.0380	80°		1.0089
20°		1.0369	75°		1.0112
25°		1.0362	70°		1.0159
30°		1.0342	65°		1.0175
40°		1.0292	60°		1.0190
50°		1.0242	55°		1.0226
60°		1.0192	50°		1.0279
70°		1.0152	40°		1.0314
75°		1.0102	30°		1.0366
80°		1.0076	25°		1.0382
85°		1.0031	20°		1.0392
90°		1.0007	15°		1.0403
			10°		1.0409
			0°		1.0414

0.1617 Molar Solution

Temp.	Violet	d	Temp.	Green	d
$0^\circ.5$		1.0612	95°		1.0162
$9^\circ.5$		1.0602	90°		1.0202
15°		1.0592	85°		1.0232
20°		1.0585	80°		1.0252
25°		1.0572	75°		1.0292
30°		1.0552	70°		1.0322
40°		1.0512	65°		1.0352
50°		1.0462	60°		1.0382
55°		1.0432	55°		1.0412
60°		1.0412	50°		1.0432
65°		1.0372	40°		1.0482
70°		1.0342	30°		1.0512
75°		1.0312			
80°		1.0262			
85°		1.0232			
90°		1.0192			

Table I—(Continued)

0.2137 Molar Solution

Temp.	Violet	d	Temp.	Green	d
20°		1.0763	85°		1.0377
25°		1.0744	75°		1.0440
30°		1.0728	65°		1.0505
40°		1.0680	55°		1.0552
50°		1.0628			
60°		1.0551			
70°		1.0493			

0.3221 Molar Solution

Temp.	Violet	d	Temp.	Green	d
21°		1.1152	85°		1.0722
25°		1.1132	80°		1.0772
30°		1.1102	75°		1.0802
40°		1.1062	70°		1.0832
50°		1.1002	65°		1.0872
55°		1.0962	60°		1.0912
60°		1.0922	55°		1.0932
65°		1.0872	50°		1.0972
70°		1.0842	40°		1.1032
75°		1.0802	30°		1.1092
80°		1.0762	25°		1.1112
85°		1.0712	21°		1.1122
90°		1.0692			

Table II.—Density

Molar conc. of violet sol.	$t = 0^\circ$	$t = 10^\circ$	$t = 20^\circ$	$t = 30^\circ$	$t = 40^\circ$
0.1024	1.0394	1.0391	1.0369	1.0342	1.0292
0.1617	1.0617	1.0602	1.0585	1.0552	1.0512
0.2137			1.0763	1.0728	1.0680
0.3221			1.1160	1.1102	1.1062
	$t = 50^\circ$	$t = 60^\circ$	$t = 70^\circ$	$t = 80^\circ$	$t = 90^\circ$
0.1024	1.0242	1.0192	1.0152	1.0076	1.0007
0.1617	1.0462	1.0407	1.0342	1.0262	1.0192
0.2137	1.0628	1.0551	1.0493		
0.3221	1.1002	1.0922	1.0842	1.0762	1.0692

These results show that with few exceptions the violet solutions are of greater density than the green solutions of the same concentration. These exceptions are, in general, among

the values obtained at high temperatures and are most marked for the solutions heated above 50° . In the solution of lowest concentration the densities of the two forms are approximately the same. Where the values for the green exceed those for the violet it is undoubtedly due to the fact that at the higher temperatures the solution lost water and, consequently, the green solution had a greater concentration than the violet.

The changes in density with varying temperature are shown in Fig. I and the changes with varying concentration in Fig. II, full lines representing the violet, and broken lines the green

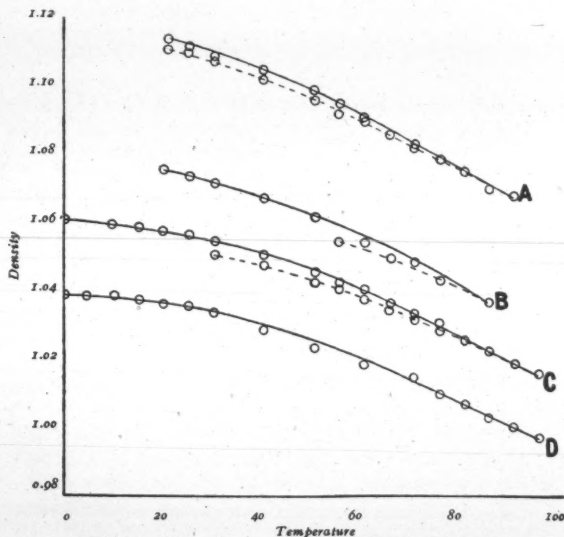


Fig. I. A, 0.3221 molar. B, 0.3137 molar. C, 0.1617 molar. D, 0.1024 molar.

solutions. Since, in Fig. II, the lines showing change of density with change of concentration are nearly parallel, straight lines, it appeared justifiable, by extrapolation, to obtain values for the density of a fifth solution not measured experimentally.

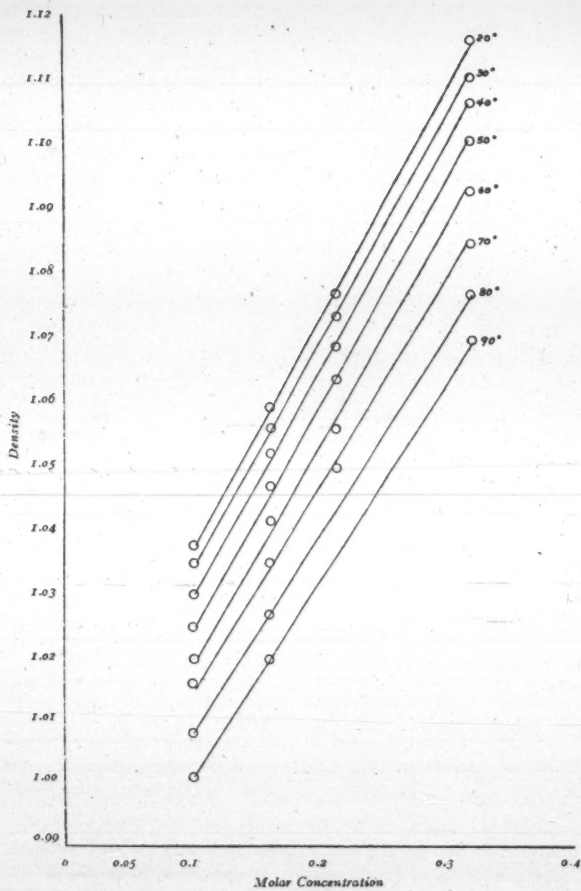


Fig. II

The curve plotted from these values is similar to those of Fig. I.

It is evident that there is no point of temperature or concentration where the density of the solutions changes suddenly, since all values for both violet and green solutions lie on smooth curves.

Viscosity

The solutions used in the measurement of viscosity were those whose densities had been determined. In these measurements the Poiseuille-Ostwald method was employed, which consists in observing, with a stopwatch, the time of flow of a definite volume of liquid, under its own pressure, between two marks on a capillary tube. Two tubes of the Ostwald-Poiseuille type were used for this purpose, a constant for each tube being determined by measuring the time of flow of a definite volume of pure water. The constants were measured at 20° and calculated from the formula,

$$K = \eta/dt$$

where t is the time of transpiration in seconds, $\eta = 0.01002$,¹ the coefficient of viscosity of water at 20°, and $d = 0.998230$,¹ the corresponding density. In measuring the viscosity of the chromium solutions a volume of the violet solution equal to the volume of water was introduced into the dry tube, and the time of flow measured as before. The coefficient of viscosity was calculated from the expression, $\eta = Kdt$, where η is the coefficient of viscosity of the solution; K , the constant of the tube; d , the density of the solution at the temperature of observation; and t , the time of transpiration in seconds.

In place of the usual thermostat a glass battery jar on a suitable stand was used for securing constant temperatures. An incandescent lamp, connected through a rheostat with an electric light circuit, served to heat the water, which was stirred by a paddle wheel run by a small electric motor. For the observations at low temperatures ice was used in the water of the bath. The tubes were clamped vertically near the center of the battery jar with the level of the water above the upper

¹ Tables of Landolt and Börnstein.

mark of the capillary. An electric light behind the stand served to illuminate the bath and was an aid in making the observations. Accurately graduated thermometers reading to tenths of a degree were used and carefully observed during each series of measurements. At temperatures in the neighborhood of 20° it was possible to keep the bath constant to within $0^{\circ}.1$, but at higher and lower temperatures this was difficult. In all determinations a series of readings was made, the temperature being read to hundredths of a degree for each measurement of the time of transpiration. The average temperature and average time were then used in the calculation of the coefficient. In general, observations were begun at the low temperatures and the bath was gradually heated in the manner described in connection with the determinations of density. Between 40° and 50° a decided change of color was noted and with falling temperature the solution did not regain its violet color. This was observed particularly in this part of the work because the electric light behind the thin layer of liquid in the capillary tube brought out the violet color more clearly.

Table III.—Viscosity
0.0501 Molar Solution

Violet		Green	
Temp.	$\eta \times 10^3$	Temp.	$\eta \times 10^3$
8°	16.78	83°	3.73
10°	15.77	78°	3.95
12°	14.82	75°	4.09
15°	13.61	70°	4.38
18°	12.69	65°	4.63
20°	11.98	$60^{\circ}.7$	5.00
25°	10.62	55°	5.32
30°	9.55	50°	5.89
40°	7.76	40°	6.88
50°	6.40	30°	8.53
60°	5.57	25°	9.46
70°	4.87	20°	10.65
77°	4.03	18°	11.19
80°	3.91	15°	12.05
		12°	13.14
		10°	14.03
		$7^{\circ}.8$	14.91

Table III—(Continued)
0.1024 Molar Solution

Temp.	Violet	$\eta \times 10^3$	Temp.	Green	$\eta \times 10^3$
3°	5	17.27	75°		4.23
20°		12.00	70°		4.53
25°		10.65	60°		5.24
30°		9.53	50°		6.13
40°		7.74	40°		7.34
50°		6.43	30°		8.98
60°		5.34	25°		10.06
70°		4.71	20°		11.34
			15°		13.03
			10°		14.93
			5°		17.30

0.1617 Molar Solution

Temp.	Violet	$\eta \times 10^3$	Temp.	Green	$\eta \times 10^3$
3°	4	21.84	77°	9	4.97
5°	8	20.26	75°	8	4.99
9°	4	18.15	70°		5.42
12°	6	16.53	65°		5.81
15°		15.46	59°	8	6.33
20°		13.55	50°		7.44
25°		12.02	40°		9.05
30°		10.76	30°		11.27
40°		8.74	25°		12.54
50°		7.87			
60°		6.59			
63°	3	6.19			
67°		5.83			
75°	9	5.12			

0.2137 Molar Solution

Temp.	Violet	$\eta \times 10^3$	Temp.	Green	$\eta \times 10^3$
7°	7	21.62	77°	6	4.80
8°	5	21.13	70°	4	5.27
9°	6	20.54	60°	6	6.04
10°	4	20.02	50°		7.23
20°		15.39°	40°		8.69
25°		13.96	30°		10.74
30°		12.06	25°		12.00
40°		9.75	20°		13.57
50°		7.95	14°		15.84
55°		7.05	13°	3	16.40
60°		6.43			
69°	7	5.51			

Table III—(Continued)

0.3221 Molar Solution

Violet		Green	
Temp.	$\eta \times 10^3$	Temp.	$\eta \times 10^3$
8°	28.94	83°	5.43
10°	27.05	80°	5.89
12°	25.63	75°	6.27
15°	23.53	70°	6.72
18°	21.87	60°	7.42
20°	20.72	50°	9.07
25°	18.27	40°	11.29
30°	16.21	30°	14.18
40°	13.01	25°	15.90
50°	10.41	20°	17.36
60°	8.47	18°	18.96
70°	7.26	15°	20.65
75°	6.27	12°	22.80
		10°	24.08

Table IV.—Viscosity

Molar conc. of violet sol.	$\eta \times 10^3$ $t = 10^\circ$	$\eta \times 10^3$ $t = 20^\circ$	$\eta \times 10^3$ $t = 25^\circ$	$\eta \times 10^3$ $t = 30^\circ$
0.0501	15.77	11.98	10.62	9.55
0.1024	...	12.0	10.65	9.53
0.1617	18.15	13.55	12.02	10.76
0.2137	20.28	15.39	13.96	12.06
0.3221	27.05	20.72	18.27	16.21
	$t = 40^\circ$	$t = 50^\circ$	$t = 60^\circ$	$t = 70^\circ$
0.0501	7.76	6.40	5.57	4.87
0.1024	7.74	6.43	5.34	4.71
0.1617	8.74	7.87	6.59	...
0.2137	9.75	7.95	6.43	5.69
0.3221	13.01	10.41	8.47	7.26

In calculating the values for the coefficient of viscosity the curves plotted for density at different temperatures were used. As might be expected from the relative densities of the two solutions, the green has less viscosity than the violet except at high temperatures, where the values are approximately the same. The change of viscosity with change of temperature is shown in Fig. III, and the change with varying concentration in Fig. IV. In Fig. III two of the solutions have been omitted to avoid confusion, because of the coincidence in each

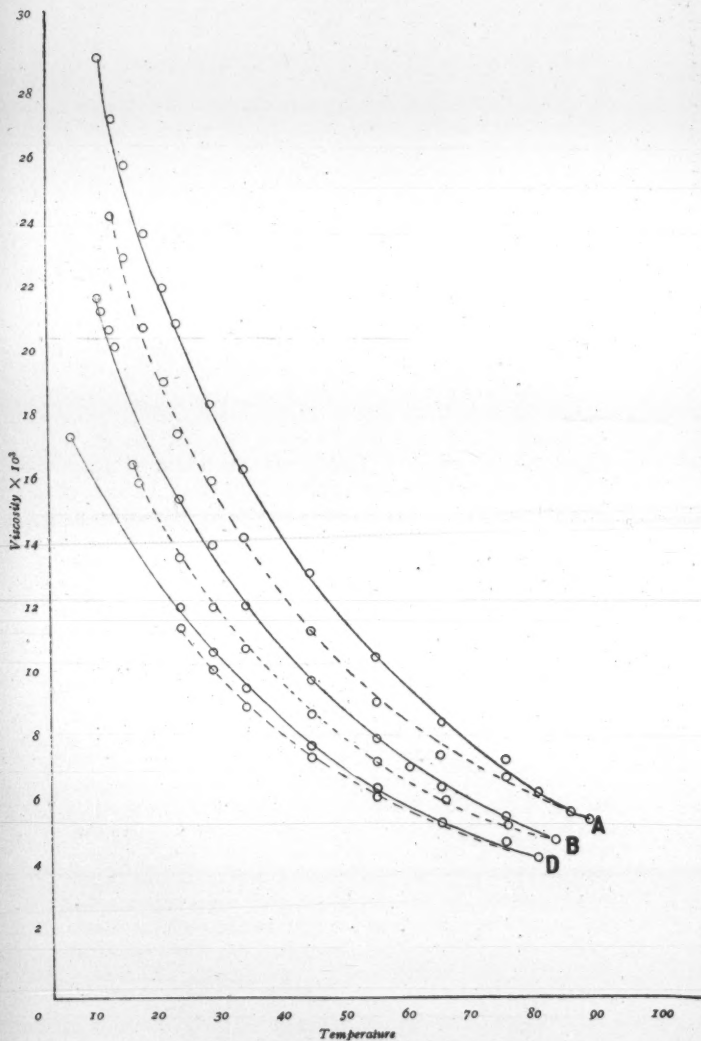
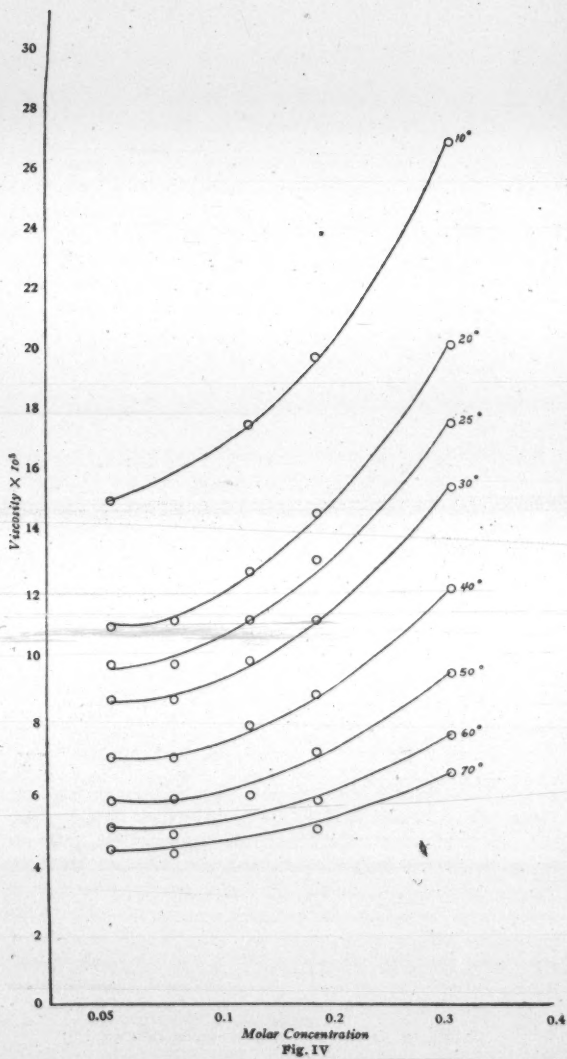


Fig. III. A, 0.3251 mol. B, 0.2137 mol. D, 0.1024 mol.



case of the curve for the violet solution with that of the green of another concentration. The curves omitted are like the others.

The curves for variations in viscosity, like those representing the densities, indicate a gradual change in the solutions with no abrupt transformation at any point. They are similar to those for violet and green solutions of chrome alum given by d'Arcey¹ in his paper on the viscosity of solutions, while the experimental results are in agreement with the conclusion of Ferrero² that the difference in viscosity of the two solutions of chrome alum becomes less as the solutions are diluted.

It was hoped that measurements of viscosity might furnish some evidence as to the rate of the reverse change from green to violet and, accordingly, after one series of measurements at different temperatures the tube was heated at 98° for several minutes and the time of flow then measured at 25° from day to day. It was only after one week that a change of one second in time of transpiration could be measured with any certainty and a second week seemed to give no measurable change.

Electrical Conductivity

The conductivity measurements were made by the method of Kohlrausch, the bridge wire having been calibrated as recommended by Strouhal and Barus. A cell of the Arrhenius type, with rather widely separated platinized electrodes, was used, and the cell constant was frequently determined by measuring the conductivity of a fiftieth-molar solution of potassium chloride. All solutions were made with water that was distilled according to the method of Jones and Mackay³ and had a specific conductivity of 1.35×10^{-6} . For work at low temperatures the cell was immersed in a battery jar filled with snow or ice, and for higher temperatures in a large thermostat heated by an incandescent bulb dipped into the bath, or, when necessary, by a gas flame underneath it. By vigorous stirring with a paddle wheel run by a motor it was possible to keep the temperature constant to 0°.1.

¹ Phil. Mag., [5] 28, 230 (1889).

² Nuovo Cimento, [5] 1, 285 (1901).

³ THIS JOURNAL, 19, 91 (1897).

For the determinations of changes in conductivity with change of temperature a violet solution of definite concentration was placed in the cell and allowed to stand in the thermostat for some time to ensure thermal equilibrium. A series of readings was then made with different resistances in the circuit and the temperature of the bath raised to the next point desired, and the process repeated until a temperature of 60° was reached. The values obtained in this way were taken to represent the conductivity of the violet solution.

Allowing the solution to remain in the cell, the bath was cooled gradually to approximately the initial temperature, and a series of observations made to obtain values for the conductivity of the green solution.

The results obtained for both solutions are given in the following tables:

Table V.—Molecular Conductivity

$v = 4680.3$ cc.

Violet		Green	
Temp.	μ	Temp.	μ
2° .5	59.36	60° .0	151.5
9° .8	72.18	55° .0	149.6
10° .8	74.2	50° .0	146.9
18° .0	92.08	40° .0	136.1
20° .0	93.21	30° .0	121.6
25° .0	101.2	25° .0	114.4
30° .0	110.6	20° .0	105.7
40° .0	125.7	18° .0	102.3
50° .0	137.6	10° .4	89.95
55° .0	143.5	0° .3	72.02

$v = 6185.6$ cc.

Violet		Green	
Temp.	μ	Temp.	μ
0° .3	77.82	60° .0	177.7
9° .3	88.47	50° .0	168.6
14° .5	98.77	40° .0	155.2
18° .0	105.2	30° .0	139.2
20° .0	109.3	25° .0	130.3
25° .0	118.9	20° .0	121.1
30° .0	128.0	18° .0	116.8
40° .0	145.3	15° .0	111.4
50° .0	159.9	11° .2	104.0
		5° .6	91.94
		2° .0	86.10

Table V—(Continued)

$v = 9765.6$ cc.

Temp.	Violet μ	Temp.	Green μ
0°.2	71.88	60°.0	187.9
9°.8	92.52	50°.0	178.9
20°.0	116.05	40°.0	162.7
25°.0	126.13	30°.0	149.2
30°.0	137.15	25°.0	140.1
40°.0	155.9	20°.0	130.6
50°.0	171.6	9°.9	111.57
		0°.0	92.79

$v = 19964.05$ cc.

Temp.	Violet μ	Temp.	Green μ
5°.0	93.93	60°.0	215.9
7°.8	103.6	50°.0	210.5
10°.5	111.0	40°.0	184.0
12°.0	114.4	30°.0	167.4
14°.8	119.5	25°.0	160.3
18°.0	127.8	20°.0	149.7
20°.0	131.5	18°.0	139.6
25°.0	143.5	15°.0	134.8
30°.0	154.8	11°.6	130.3
40°.0	178.7	9°.8	124.4
50°.0	189.3	7°.8	115.9
		5°.0	111.5

Table VI.—Molecular Conductivity
Violet Solution

v (cc.)	μ $t = 10^\circ$	μ $t = 20^\circ$	μ $t = 25^\circ$	μ $t = 30^\circ$
4680.3	72.18	93.21	101.2	110.6
6185.6	88.47	109.3	118.9	128.0
9765.6	92.52	116.05	126.13	137.15
19964.05	111.0	131.5	143.5	154.18
	$t = 40^\circ$	$t = 50^\circ$	$t = 60^\circ$	
4680.3	125.7	137.6	151.5	
6185.6	145.3	159.9	177.7	
9765.6	155.9	171.6	187.9	
19964.05	178.7	189.3	215.9	

Table VI—(Continued)

Green Solution

v (cc.)	$t = 10^{\circ}.5$	$t = 20^{\circ}$	$t = 25^{\circ}$
4680.3	88.0	105.7	114.4
6185.6	102.0	121.1	130.3
9765.6	111.57	130.6	140.1
19964.05	124.4	149.7	160.3
	$t = 30^{\circ}$	$t = 40^{\circ}$	$t = 50^{\circ}$
4680.3	121.6	136.1	146.9
6185.6	139.2	155.2	168.6
9765.6	149.2	162.7	178.9
19964.05	167.4	184.0	210.5

Curves showing the changes in molecular conductivity with temperature are plotted in Fig. V, and those showing change in molecular conductivity with change in volume in Fig. VI. The conductivity of the green solution is for all temperatures and all concentrations higher than that of the corresponding violet solution.

As the solutions had not been heated to as high a temperature as in the density and viscosity experiments, two of the solutions were afterwards heated in closed flasks in a bath of boiling water for fifteen minutes and the conductivity then measured at 20° . The value obtained was considerably higher than the first value for the green solution at 20° . The conductivity of this solution slowly dropped when it was kept at 20° . The decrease was perceptible after a few hours and became more marked as the observations were continued. An attempt was made to apply one of the kinetic equations to establish the order of the reverse reaction, but the values calculated for a constant were not satisfactory. The investigation of this feature of the problem has not been continued, but it is hoped that by using the improved method of preparing the green solutions which was adopted later it will be possible to secure some interesting data on the change of green solutions to violet.

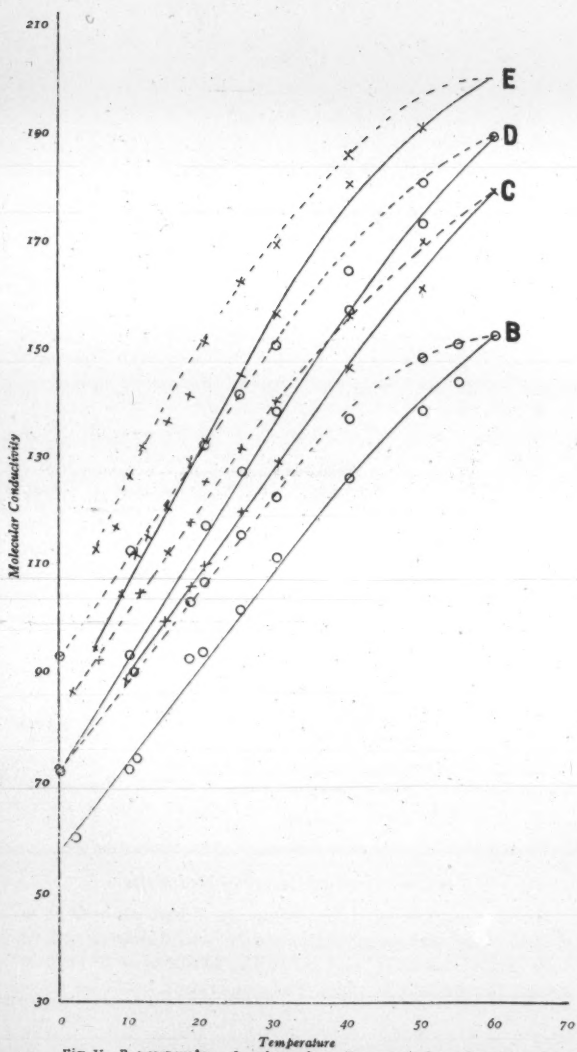


Fig. V. B, 0.2137 molar. C, 0.1617 molar. D, 0.1024 molar. E, 0.0501 molar.

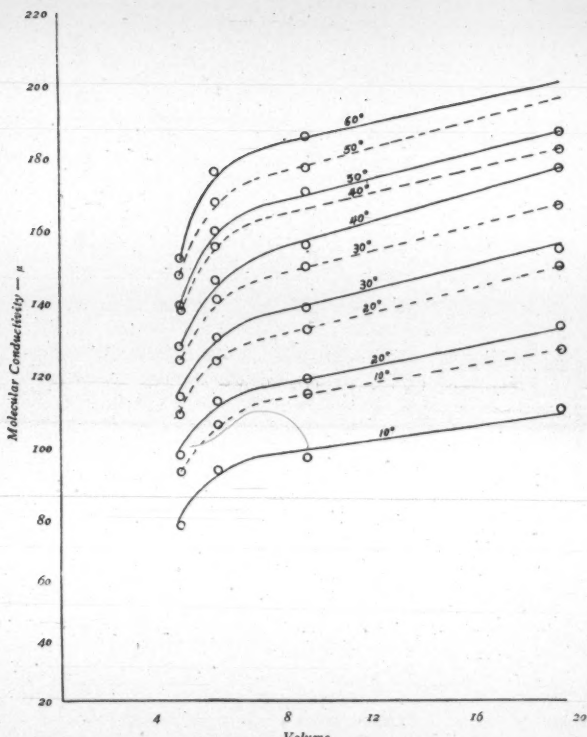


Fig. VI

Conductivity as a Measure of Hydrolysis

For the purpose of determining the extent of hydrolysis of both violet and green solutions very careful determinations were carried out at 0° and 25°. The solutions were kept in special thermostats in which the temperature could be accu-

rately controlled. Each thermostat consisted of two concentric galvanized iron tanks, the annular space between them being filled with sawdust. One bath was kept at 25° by using an Ostwald thermoregulator, connected with a telegraphic relay, the water being heated by an incandescent lamp and well stirred. A thermometer specially calibrated for 25° was used and the temperature was constant to $0^{\circ}.1$. The zero bath was well filled with crushed ice and it was possible, by stirring thoroughly, to keep the temperature at $0^{\circ}.1$ for six or seven hours.

A sixteenth-molar solution of the violet salt was prepared by weighing the necessary quantity, which was calculated from the actual content in chromic oxide as determined by analysis, dissolving it in ice-cold conductivity water and diluting as usual at room temperature. This solution was used immediately and carried through the customary series of dilutions for conductivity measurements, readings at zero being made before those at 25° . In the same way measurements were made upon a green solution prepared from the initial violet solution by heating the latter for an hour in a pressure bottle placed in a bath of boiling water. This method of preparation of the green solution is more satisfactory than the methods used heretofore, as change of concentration by loss of solvent is avoided.

Table VII gives the results obtained in this series of measurements, and curves showing increase in conductivity with increasing dilution are plotted in Fig. VII:

Table VII.—Molecular Conductivity

$t = 0^{\circ}$			
Violet		Green	
V	μ	V	μ
16	85.37	16	168.1
32	100.0	32	187.7
64	117.70	64	211.2
128	139.20	128	233.2
256	166.60	256	255.2
512	194.2	512	270.8
1024	232.2	1024	282.1

Table VII—(Continued)

 $t = 25^{\circ}$

Violet		Green	
V	μ	V	μ
16	151.5	16	245.7
32	177.1	32	285.2
64	211.8	64	336.5
128	255.0	128	390.4
256	310.2	256	450.7
512	379.5	512	515.0
1024	476.9	1024	568.5

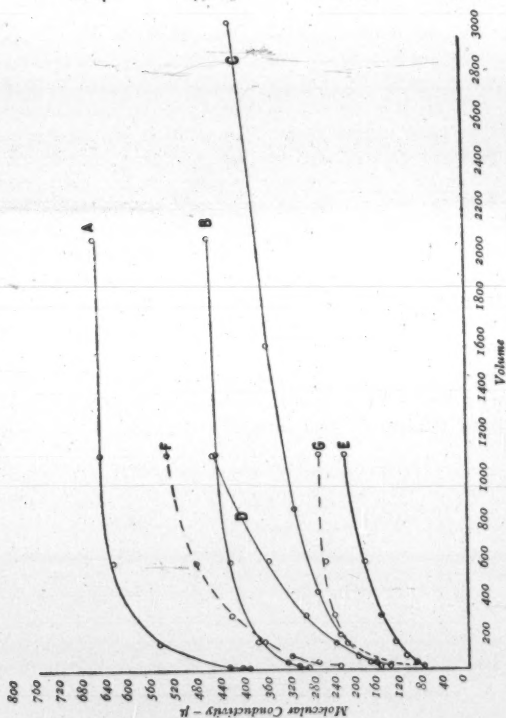


Fig. VII. A, sulphuric acid at 25° . B, sulphuric acid at 0° . C, lanthanum sulphate at 25° . D, violet solution at 25° . E, violet solution at 0° . F, green solution at 25° . G, green solution at 0° .

The curve for the green solution at 0° is of interest as it indicates a tendency to return to the violet modification at this temperature. For the sake of comparison I have plotted also results of Jones and Douglas¹ and Jones and West,² showing the molecular conductivity of sulphuric acid at 0° and 25° , and a curve showing the molecular conductivity at 25° of lanthanum sulphate, an unhydrolyzed salt. The points for this last curve were obtained by calculating values for molecular conductivity from the values for equivalent conductivity published by Muthmann.³ The molar concentrations used by Muthmann are not the same as those used with the chromium sulphate, but by plotting the curve on a large scale it was possible to get the corresponding points with sufficient accuracy for comparison.

The amount of hydrolysis was calculated by the method originally proposed by Ley.⁴ This is based on the difference in conductivity caused by diluting equivalent solutions of hydrolyzable and unhydrolyzable salts having a common ion. As was first shown by Ostwald,⁵ normally dissociated salts show nearly constant differences in the values of the equivalent conductivity at two given dilutions. The difference between the values obtained by similarly diluting hydrolyzable salts is, of course, greater, because the total number of ions is increased by hydrolysis, and Ley proposes to take advantage of this fact for calculating the amount of hydrolysis. For this purpose he applies the formula

$$X = \frac{L - \mu_1}{\mu_2 - \mu_1}$$

where μ_1 is the conductivity of the unhydrolyzed salt, μ_2 that of the acid formed by hydrolysis, and L the conductivity measured by experiment. For each dilution, for which the degree of hydrolysis is to be calculated, it is necessary to find a value, μ_1 , to represent the conductivity of the unhydrolyzed salt. This is accomplished as follows: The value μ_1 for the

¹ THIS JOURNAL, **26**, 436 (1901).

² *Ibid.*, **34**, 415 (1905).

³ Ber. d. chem. Ges., **31**, 1834 (1898).

⁴ Z. physik. Chem., **30**, 193 (1899).

⁵ Lehrbuch der allgem. Chem. (2 Aufl.), **2**, 650.

most concentrated solution is obtained by determining the conductivity of this solution; on the assumption that there is no hydrolysis at this concentration, $\mu_1 = L$. The values for the more dilute solutions are found by measuring the increase in conductivity caused by diluting a corresponding solution of a normally dissociated salt having the same anion and a similar constitution, and adding this increment to the initial μ_1 of the salt under investigation. Thus, assuming that there is no hydrolysis in a given salt when $V = 16$, and representing the increase in conductivity caused by diluting an analogously constituted normal salt from $V = 16$ to $V = 32$ by Δ , Ley's formula becomes:

$$X_{32} = \frac{L_{32} - (\mu_{16} + \Delta)}{\mu_2 - (\mu_{16} + \Delta)}$$

In the case in hand lanthanum sulphate was used as the accessory salt, because it is constituted like chromium sulphate, but according to Muthmann is not hydrolyzed in aqueous solution. The following example shows how the amount of hydrolysis of different solutions of chromium sulphate was calculated.

The conductivity of the violet solution at 25° was found, experimentally, to be 151.5 when $V = 16$, and 177.1 when $V = 32$; the value of $\Delta (V_{32} - V_{16})$ for lanthanum sulphate, taken from the curve, is 15; and the value of $\mu_2 = \mu_\infty$ for sulphuric acid at 25° is 705: therefore, $X_{32} = \frac{177.1 - 166.5}{705 - 166.5}$.

Table VIII.—Hydrolysis at 25°

V	μ for $\text{La}_2(\text{SO}_4)_3$	Δ	Percentage of hydrolysis of chromium sulphate	
			Violet	Green
16	139	...	...	17.02
32	154	15	1.78	22.04
64	183	44	3.19	27.68
128	220	81	4.76	33.42
256	263	124	8.08	40.74
512	304	165	16.24	51.10
1024	347	208	33.98	60.49

Table VIII gives the data used in the calculations and Fig. VIII shows the curves representing the hydrolysis of the green

and violet solutions. The values for the hydrolysis, calculated by Ley's method, are less for both solutions than those obtained by Denham¹ from measurements of potential, though

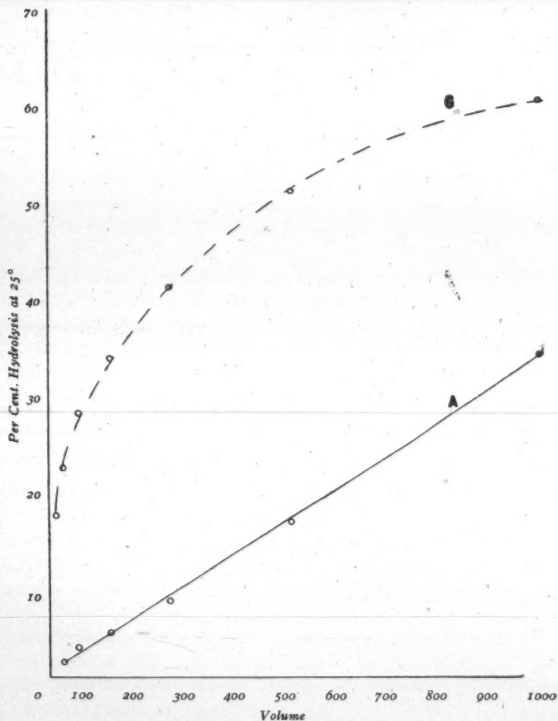


Fig. VIII. A, violet. G, green.

the ratios between values for corresponding green and violet solutions are similar to the ratios of Denham's values for the same concentration.

¹ *Loc. cit.*

Catalytic Action as a Measure of Hydrolysis

The extent of the hydrolysis in solutions of chromic sulphate was studied in 1903 by Richards and Bonnet,¹ who acted upon the suggestion of Long² that the green solution of chromium sulphate, but not the violet, might be expected to cause inversion of cane sugar. They measured the speed of inversion produced by each of the solutions at approximately 17° and 30°, and estimated the amount of ionized hydrogen in the green solutions under investigation. Owing to the deep color of the solutions the polarimetric method of determining the rate of inversion could not be used, but Richards and Bonnet resorted to a method which had been developed by Kahlenberg, Davis, and Fowler.³ This method is based upon the fact that the depression of the freezing point of water caused by invert sugar is approximately twice as great as the depression produced by the cane sugar from which the invert sugar is formed. Assuming that the catalyzing agent used for the inversion has a constant influence upon the freezing point, it is possible to follow the course of inversion by measuring, at frequent intervals, the depression of the freezing point, the point of complete inversion being reached when there is no further increase in the depression. I used the same method.

After some preliminary work at about 18° for the purpose of testing the method of procedure of Richards and Bonnet and finding, as they did, that the violet solution produced very little inversion at 18°, I decided to continue the work at a higher temperature and under somewhat different conditions.

A sugar solution was made by dissolving 250 grams of pure rock candy per liter of conductivity water. This solution was sterilized by prolonged heating in a water bath at 100°, and protected from ferments that might cause inversion by addition of a crystal of thymol, as recommended by Morse⁴ in his work on osmotic pressure.

¹ *Loc. cit.*

² *J. Am. Chem. Soc.*, **19**, 683 (1897).

³ *Ibid.*, **21**, 1 (1899).

⁴ *THIS JOURNAL*, **36**, 37 (1906).

Violet solutions of chromium sulphate of two-tenths and one-tenth molar concentration were prepared by dissolving the calculated weight of salt in cold conductivity water and from these the green solutions were obtained by heating for an hour in a pressure bottle in a bath of boiling water. The violet solutions were kept in an ice chest until needed and the green solutions were used as soon as they had been cooled to room temperature.

Equal volumes of the sugar solution and conductivity water were mixed and kept as a standard solution from which to calculate changes in depression of the freezing point. Similarly, equal volumes of the original sugar solution and a solution whose catalyzing effect was to be measured were mixed and kept in well corked test tubes which were suspended in a wire rack in a thermostat kept at approximately 30° .

In order to prevent catalytic action as much as possible the solutions were mixed in tubes immersed in ice or snow. After determining the freezing point of a mixture the tube was placed in a thermostat for a few hours, when another determination was made, this procedure being continued for several days.

The measurements of the freezing points were made with the Beckmann apparatus. The zero point of the thermometer and the freezing point of the standard sugar solution were determined at frequent intervals. In the preliminary experiments, the calculations of depression were based upon the freezing point of the sugar solution, but it seemed better in the later work to measure the depressions for all solutions directly from the freezing point of water as registered by the thermometer at the time of the experiment.

At 30° the inversion proceeded much more rapidly than at 18° , and the violet solutions were evidently hydrolyzed, a distinct change of color being noticeable as well as an increase in the depression of the freezing point.

Observations were made not only on the fresh violet and green solutions, but also on a two-tenths molar green solution which had been kept at 30° in the thermostat for two weeks,

a one-tenth molar violet solution kept at room temperature for one month, a one-tenth molar green solution dehydrolyzed in an ice chest for one week, a similar solution dehydrolyzed at room temperature for fifty days, and a 0.1105 normal solution of sulphuric acid.

The results are given in Table IX. Column *K* gives the coefficients for the speed of inversion, calculated according to the equation

$$K = \frac{1}{t} \log_e \frac{a}{a-x}$$

where *a* is the initial concentration of the cane sugar solution and *x* the amount inverted in the time *t*. For *a* may be substituted Δ , the depression of the freezing point due to cane sugar alone ($0^\circ.820$), and for *x* the increase in the depression during time *t*. Transforming to ordinary logarithms and substituting, the expression becomes

$$0.4343 K = \frac{1}{t} \log_{10} \frac{\Delta}{\Delta - (\Delta_2^1 - \Delta_1^1)}$$

Table IX.—Catalytic Action at 30°

Δ^1 = depression of freezing point of water corrected for supercooling. $\Delta_2^1 - \Delta_1^1$ = increase in depression in time *t*.

$$K = \frac{1}{0.4343 t} \log_{10} \frac{\Delta}{\Delta - (\Delta_2^1 - \Delta_1^1)} \quad (\Delta = 0^\circ.820)$$

	Violet solution. 0.2 Molar.		Fresh
<i>t</i> (hours)	Δ^1	$\Delta_2^1 - \Delta_1^1$	<i>K</i>
0.0	1.332	0.0	
16.0	1.410	0.078	0.006232
18.0	1.406	0.074	0.005257
42.5	1.607	0.275	0.009601
46.5	1.627	0.295	0.009576
69.5	1.683	0.351	0.008772
87.5	1.819	0.487	0.010300
140.0	1.977	0.645	0.011040
164.0	2.032	0.700	0.011710
			0.009061

Table IX—(Continued)

Green solution. 0.2 Molar. Fresh			
t (hours)	Δ^1	$\Delta_2^1 - \Delta_1^1$	K
0.0	1.387	0.0	
3.0	1.532	0.145	0.06463
5.0	1.577	0.190	0.05259
24.0	1.890	0.503	0.03960
28.5	1.936	0.549	0.05500
45.5	2.041	0.654	0.03510
47.5	2.036	0.649	0.03300
68.5	2.024	0.637	0.02200
92.5	2.062	0.675	0.01873
140.0	2.055	0.668	0.01217
166.0	2.073	0.686	0.01091
0.03437			
Violet solution. 0.1 Molar. Fresh			
t (hours)	Δ^1	$\Delta_2^1 - \Delta_1^1$	K
0.0	1.094	...	
16.5	1.146	0.052	0.003963
21.5	1.152	0.058	0.003406
39.5	1.218	0.124	0.004122
63.5	1.304	0.210	0.004659
87.5	1.368	0.274	0.004647
135.0	1.461	0.367	0.004395
148.5	1.583	0.489	0.006108
152.5	1.546	0.452	0.005255
190.0	1.630	0.536	0.005454
0.004667			
Green solution. 0.1 Molar. Fresh			
t (hours)	Δ^1	$\Delta_2^1 - \Delta_1^1$	K
0.0	0.976	...	
3.0	1.005	0.029	0.011198
5.0	1.032	0.056	0.01414
23.0	1.267	0.291	0.01905
26.0	1.300	0.324	0.01933
46.5	1.434	0.458	0.01758
70.5	1.521	0.545	0.01550
99.5	1.608	0.632	0.01480
118.5	1.620	0.644	0.01298
168.5	1.664	0.688	0.01084
0.01402			

Table IX—(Continued)

Green solution. 0.2 Molar. Dehydrolyzed at 30° for 2 weeks

<i>t</i> (hours)	Δ^1	$\Delta_2^1 - \Delta_1^1$	<i>K</i>
0.0	1.373	...	
3.0	1.457	0.084	0.03600
23.0	1.746	0.373	0.02638
46.0	1.935	0.562	0.02514
75.0	2.058	0.685	0.02405
95.0	2.094	0.721	0.02225
142.5	2.132	0.759	0.01823
			0.02534

Violet solution. 0.1 Molar. Hydrolyzed at room temperature for 1 month

<i>t</i> (hours)	Δ^1	$\Delta_2^1 - \Delta_1^1$	<i>K</i>
0.0	1.099	...	
25.0	1.241	0.142	0.006043
49.0	1.333	0.234	0.006857
77.5	1.480	0.381	0.008061
97.5	1.548	0.449	0.008108
145.5	1.689	0.590	0.008736
			0.007561

Green solution. 0.1 Molar. Dehydrolyzed in ice chest for 1 week

<i>t</i> (hours)	Δ^1	$\Delta_2^1 - \Delta_1^1$	<i>K</i>
0.0	0.970	...	
5.0	1.050	0.080	0.02053
25.5	1.257	0.287	0.01690
29.5	1.286	0.316	0.01650
48.5	1.406	0.436	0.01564
71.5	1.494	0.524	0.01425
99.0	1.570	0.600	0.01329
			0.01619

Table IX—(Continued)

Green solution. 0.1 Molar. Dehydrolyzed at room temperature for 50 days

<i>t</i> (hours)	Δ^1	$\Delta_2^1 - \Delta_1^1$	<i>K</i>
0.0	1.136	...	
23.0	1.415	0.279	0.01808
41.0	1.534	0.398	0.01620
69.0	1.649	0.513	0.01424
92.5	1.724	0.588	0.01365
112.0	1.782	0.646	0.01385
165.0	1.807	0.671	0.01034
187.0	1.817	0.681	0.00949
			0.01369

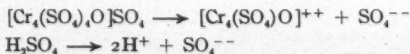
Sulphuric acid. 0.1105 Normal

<i>t</i> (hours)	Δ^1	$\Delta_2^1 - \Delta_1^1$	<i>K</i>
0.0	0.953	0.0	
2.0	1.022	0.069	0.04398
5.0	1.088	0.135	0.03596
24.0	1.381	0.428	0.03075
48.0	1.586	0.633	0.03080
53.5	1.609	0.656	0.03008
73.0	1.657	0.704	0.02679
94.0	1.687	0.734	0.02399
144.0	1.695	0.742	0.01633
169.0	1.687	0.734	0.01335
			0.02800

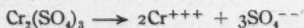
The inversion caused by sulphuric acid was determined for purposes of comparison. By means of similar measurements with hydrochloric acid, Richards and Bonnet estimated the number of atoms of chromium corresponding to one ion of hydrogen in the green solution.

A comparison of the coefficients for the velocity of inversion at 30° shows that the 0.2 molar violet solution catalyses nearly one-third as rapidly as the 0.1105 normal sulphuric acid solution while the corresponding green solution has a catalyzing action 1.22 times as great as the acid. According to the method of calculation of Richards and Bonnet, the green solution must contain as much ionized hydrogen as a 0.135 normal or 0.0675 molar solution of sulphuric acid. From a com-

parison of the relative velocities during the first part of the inversion, it is evident that the violet solution has about one-seventh the effect of the acid while the green is one and one-half times as active. The comparison of the other constants is also of interest. The two-tenths molar violet solution is nearly twice as active as the fresh one-tenth molar solution, but not much more active than the one-tenth molar solution hydrolyzed for one month at room temperature. On the other hand, the mean coefficient for the fresh one-tenth molar green solution is less than that of the same solution dehydrolyzed in the ice chest for one week and not much greater than that of the same solution dehydrolyzed at room temperature for fifty days. This is contrary to expectation but must be attributed to changes in concentration and in ionization which occur during hydrolysis and dehydrolysis. It will be seen from Table IX that the solution in question depresses the freezing point less at first than the corresponding violet solution but that the speed of inversion is greater. This cannot be due to experimental error because the work was repeated and verified. The green solution has a smaller density than the corresponding violet solution and, consequently, there is actually less of the salt present in a given volume; but the difference in concentration is too small to account for the results. Undoubtedly the number of ions in solution must also be taken into account in explaining these variations. For complete hydrolysis the ionic condition may be represented as follows:



When hydrolysis is not complete there are present also the ions of chromium sulphate and therefore the total number is greater:



The mean coefficients have been collected in Table X and the percentage of hydrolysis calculated according to Kahlenberg's¹ method. For the calculation, the percentage of dis-

¹ *Loc. cit.*

sociation of 0.055 normal sulphuric acid at 30° has been obtained by interpolation from curves plotted from the values of Jones and West.¹ The acid is taken as 0.055 normal and the chromium solutions as 0.1 and 0.05 molar, respectively, because of the dilution when the mixtures with the sugar solution are made. The percentages calculated must be regarded as rough approximations of the amount of hydrolysis in chromium solutions when sugar is present. They serve merely to give some idea of the relations of the violet and green solutions and of different concentrations of the same solution:

Table X.—Hydrolysis at 30°

Solution	K	Percentage of hydrolysis
0.2 Molar violet (fresh)	0.009061	2.21
0.2 Molar green (fresh)	0.03437	8.39
0.1 Molar violet (fresh)	0.004667	2.28
0.1 Molar green (fresh)	0.01402	6.84
0.2 Molar green (2 weeks old)	0.02534	6.18
0.1 Molar violet (1 month old)	0.007561	3.69
0.1 Molar green (1 week old)	0.01619	7.90
0.1 Molar green (50 days old)	0.01369	6.68
0.1105 Normal H ₂ SO ₄	0.02800	

The increase in the depression with time is plotted in Fig. IX. Curves for the violet solutions indicate a steady increase in catalytic action, while those for the green solutions are similar to the curve for the acid, rising rapidly to a maximum and becoming practically horizontal. The curves for the dehydrolyzed green solutions have characteristics in common with the fresh green and fresh violet solutions of corresponding concentration, but there is greater difference between the curves of the fresh violet (0.1 molar) and the same solution kept for one month at room temperature than there is between the curves for the 0.1 molar green solution. It is evident that the change from violet to green takes place much more rapidly at room temperature than does the reverse process, as the three curves for the one-tenth molar green solution are nearly coincident.

¹ *Loc. cit.*

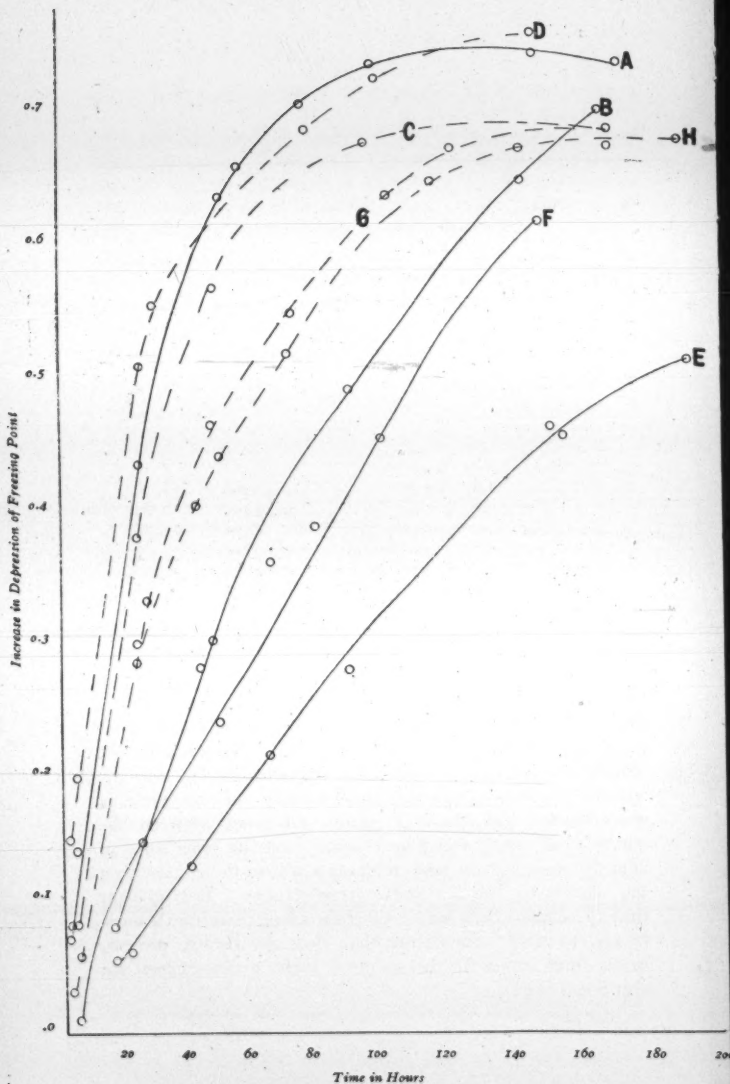


Fig. IX. Temperature, 30° . A, sulphuric acid, 0.1105 normal. B, violet solution, 0.3 molar. C, green solution, 0.3 molar (fresh). D, green solution, 0.3 molar (old). E, violet solution, 0.1 molar (fresh). F, green solution, 0.1 molar (old). G, green solution, 0.1 molar (fresh). H, green solution, 0.1 molar (old).

The experimental points for the violet solutions seem to indicate at times a condition of unstable equilibrium. This may be due to a tendency of the partially hydrolyzed solution to return to the unhydrolyzed condition at low temperatures, as fluctuations were frequently observed, causing difficulty in obtaining the true freezing points of the violet solutions. From this fact and from a comparison of the curves the conclusion may be drawn that at ordinary temperatures the green solution is more stable than the violet.

Absorption Spectra

A number of investigators have been interested in the absorption phenomena exhibited by solutions of chromium salts, including those of the sulphate. An admirable account of the literature and a bibliography of the subject are given by Jones and Anderson in their recent work, "The Absorption Spectra of Solutions."¹ An examination of this literature shows that little has been done in comparing the effects produced by violet and green solutions of the same concentration.

In comparing these solutions I have made both visual and photographic observations, using a Hilger spectroscope (mean deviation type) for visual measurements and for photographing the visible region of the spectrum, and a Fuess spectrograph, fitted with a quartz prism and quartz lenses, for work in the ultraviolet region.

The Hilger spectroscope used was similar to the instrument described by Jynes² and a Nernst filament was used as a source of light. After some preliminary tests a 0.025 molar solution of the violet salt was chosen for visual observation. A small Baly tube was used, the thickness of solution being fixed at one centimeter. A marked band of absorption was observed from λ 6400 to λ 5400 with general absorption at λ 7600 and λ 4700. The bands were measured by bringing the cross-hairs in focus upon first one edge and then the other of the colored bands observed in the red and blue regions, the

¹ Carnegie Institution of Washington: Publication No. 110 (1909).

² *Hydrates in Aqueous Solution*, p. 171. Carnegie Institute of Washington: Publication No. 60 (1907).

wave lengths being read from the drum of the instrument. The visual work was merely preliminary to the photographic observations which follow and was not extended.

In using the Hilger spectroscope for photographic work the telescope was replaced by a camera. A Nernst filament was put in circuit with an ammeter and the current kept nearly constant at 0.8 ampere by means of a rheostat. A large Baly tube, provided with quartz ends and having a range of ten centimeters, was used for the solutions, the light of the Nernst filament was brought to a focus upon the slit by means of a quartz lens, and the tube of solution was then placed lengthwise between the filament and the lens. The width of slit was 0.2 mm. and the time of exposure two minutes. Sensitive panchromatic plates made by the M. A. Seed Company were used, and ten exposures made with a given solution in the tube, beginning with a thickness of ten centimeters. For purposes of reference the spectrum of hydrogen was photographed on each plate and on some plates also the spectra of mercury and helium.

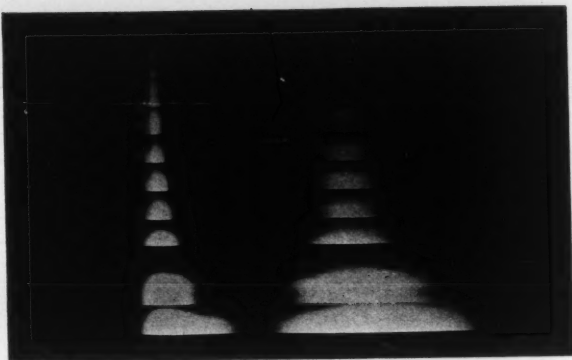
The violet and green solutions used were 0.025 and 0.0125 molar. The 0.025 molar violet solution was made by weight in the usual manner, the 0.0125 molar solution was prepared from it by dilution, and the green solutions were made by heating the corresponding violet solutions in pressure bottles for an hour in a bath of boiling water—they were used immediately after preparation.

The difference in the absorption effects of the violet and green solutions is quite evident in Plates I and II. The band due to the green solution is much broader than that produced by the violet and the general absorption is greater. A comparison of Plates I and II shows the effect of dilution upon the absorbing power of the solutions.

In Plate IA the band lies between λ 6563 and λ 4861 with general absorption beginning at λ 4700. In IB the absorption for the first four exposures is general up to λ 5016 and the widest part of the band is between λ 6563 and λ 5048 with general absorption at λ 4861. In Plate II the bands are narrower, falling between λ 5900 and λ 5100 in A, and between

Violet

A



Hydrogen

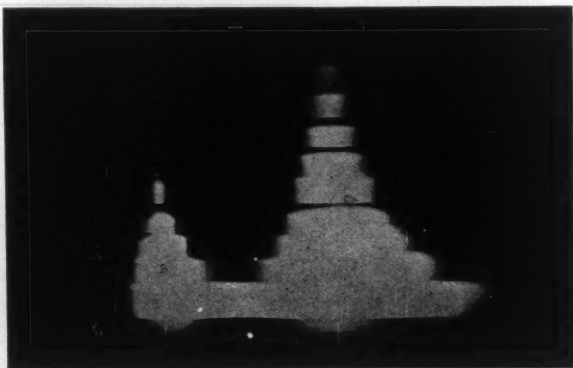
6563

4861

4341

Green

B



Hydrogen

Mercury

6563

4861

4358

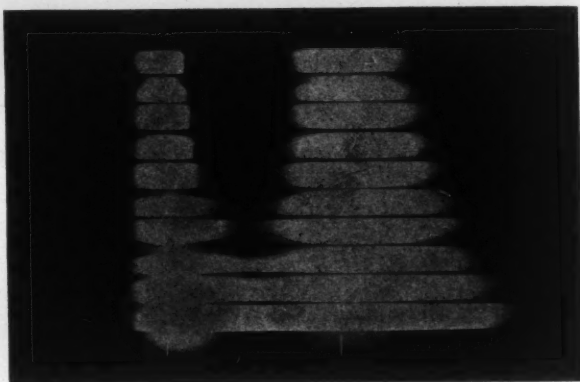
4341

PLATE I

0.025 Molar

Violet

A



Hydrogen

Mercury

6563

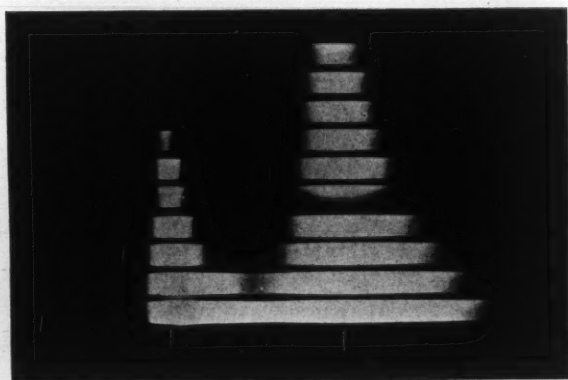
4861

4158

4341

Green

B



Hydrogen

Helium

6678
6683

5475

5448
5016
4922
4861
4713

4478
4384
4341

PLATE II

0.0135 Molar



Helium

6678

5876

5016

4922

4713

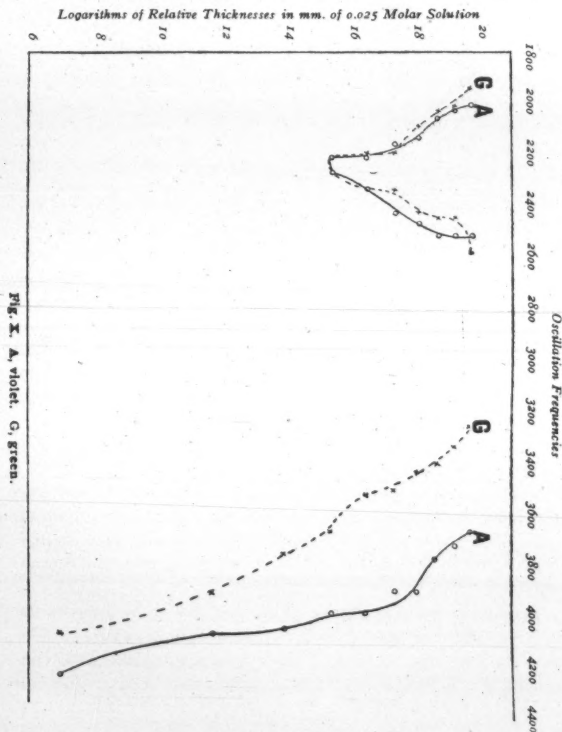
4472

4384

PLATE III

λ 6563 and λ 5048 in B, with general absorption at λ 4400 and λ 4600 in A and B, respectively. Plate III is given to show the effect of the sensitizing dye upon the absorption in the green.

For work in the ultraviolet a copper arc, connected with an electric light circuit, served as the source of light. The large Baly tube used in the preceding work was placed between the copper arc and the quartz lens which focussed the light upon the slit of the spectrograph.



Violet and green solutions of 0.025 molar concentration were measured, the thickness being varied from ten centimeters to one. The spectrum of copper was photographed upon each plate for comparison.

A distinct band is observed in the ultraviolet region and a difference similar to that observed in the visible region is noted for the two solutions.

From measurements of the lines in the spectrum of copper the absorption bands for the two solutions were determined, the results being plotted in Fig. X, where the oscillation frequencies are abscissas, and logarithms of the thickness of solution are the ordinates. From these curves it appears that the greater difference between the two solutions is in the region of general absorption, the other boundary of this band being shown in Plate I.

SUMMARY

The results of this research may be summarized as follows:

1. The yield of violet chromic sulphate from chromic acid is increased by carrying out the reduction at low temperatures, by allowing considerable time for deposition of the salt, and by keeping all solutions as cold as possible during the processes of purification.
2. Solutions of the violet salt are not stable at room temperature and the results of any measurements are more reliable if the solutions are kept at a low temperature until needed for the experiments.
3. Measurements of density, viscosity and electrical conductivity indicate that a gradual change occurs as the violet solution becomes green with increasing temperature, and that the reverse change with falling temperature is also a gradual one. The same conclusion holds with reference to the changes that occur in the two solutions when the concentrations are varied.

Assuming that the change in color is due to hydrolysis, the conclusion to be drawn, from the changes in density, viscosity and conductivity, is that for each temperature and each concentration there is a condition of equilibrium between the violet and green modifications.

4. The hydrolysis, as determined by measurements of conductivity, is evidently increased in both solutions by dilution. Measurements of the conductivity of the violet solution at zero indicate a small amount of hydrolysis which becomes measurable with increasing dilution, and a tendency of the green solution to become dehydrolyzed at the low temperature.

5. By comparing the catalytic effect produced by the chromium solutions with that due to a standard solution of sulphuric acid the hydrogen ion concentration of a given solution can be estimated and from this the percentage of hydrolysis can be roughly calculated.

Catalytic measurements with corresponding solutions of different ages indicate that the change from violet to green is much more rapid than the reverse process.

6. Observations of the absorption effects caused by the solutions indicate that the change in color in chromium sulphate solutions is not due to simple hydrolysis, but is the result of a process that involves both hydrolysis and change in structure.

7. All of the measurements and the calculations of hydrolysis lead to the conclusion that the reaction to which the change of color is due does not take place in successive steps involving the formation of a number of intermediate compounds, but that it is a single process tending to an equilibrium defined by the variables time, temperature and concentration.

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BRYN MAWR COLLEGE
June, 1912

A CHRONOLOGICAL BIBLIOGRAPHY OF THE CHANGE FROM VIOLET TO GREEN
IN CHROMIUM SULPHATE

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REVIEWS

TECHNICAL METHODS OF CHEMICAL ANALYSIS. Edited by GEORGE LUNGE, PH.D., DR. ING., Emeritus Professor of Technical Chemistry, Federal Polytechnic School, Zurich. English translation from the latest German edition, adapted to English conditions of manufacture. Edited by CHARLES ALEXANDER KEANE, D.Sc., PH.D., Principal and Head of the Chemical Department, The Sir John Cass Technical Institute, London. Volume II, Part I, xxvii + 610 pp., and Part II, xii + 641 pp. New York: D. Van Nostrand Company. 1911. \$12.00.

To review adequately a volume of such enormous size, of so many subjects, and involving so much detail would require much more space than is ordinarily granted to such a review. Indeed, it is doubtful whether it would be profitable unless the reviewer were to associate with him as many readers expert in their line as the German and English editors have associated with them. That such a work should be successful necessarily involves the association of a large number of experts in special fields. The names of both the German and English sub-editors is evidence of the good intentions of the publishers. The list of the subjects treated is not large, considering the size of the two parts constituting the volume. Iron, including ores, iron and steel analysis, metals other than iron, and metallic salts, artificial manures, feeding stuffs, explosives, matches and fireworks, calcium carbide and acetylene, illuminating

gas and ammonia, coal tar, and organic dyes are the subjects treated. These subjects alone do not adequately represent the contents. For instance, under the title, "Metals Other than Iron," are given methods of analysis, in nearly all cases including the latest information, of all the ores and the technically useful metals. The number of pages devoted to this chapter is 284. To organic dyes is given 341 pages.

To anyone doing general work and not having available a first-class working library this book would be invaluable.

H. F.

A DICTIONARY OF APPLIED CHEMISTRY. By SIR EDWARD THORPE, C.B., LL.D., F.R.S., Professor of General Chemistry and Director of the Chemical Laboratories of the Imperial College of Science and Technology, South Kensington, London, assisted by Eminent Contributors. In Five Volumes. Revised and Enlarged Edition, with Illustrations. Vol. I, A-Che. London, New York, Bombay and Calcutta: Longmans, Green & Co. 1912. pp. viii + 758. Price, \$13.50.

That a new and modernized edition of this well known work will soon be ready is welcome news to all chemists and engineers having to deal with industrial chemical problems. The original edition of 1890-1893 found a place in nearly every library and works' laboratory and few books of reference have had such frequent use. The concise and handy form in which the information is presented won for the book a high place in the regard of all manufacturing chemists. Every new question in the factory procedure would send the chemist and engineer to the "Dictionary" for information concerning the matter. But in the twenty odd years since the original issue, many new substances which have become common articles of commerce, such as the important and interesting electric furnace products, and processes which are now firmly established industrially, could not be found in the "Dictionary," while information relating to many other subjects was meager or entirely out of date. It is, therefore, a matter of satisfaction to find such complete treatment of abrasives, including carborundum and alundum, of acetylene as an illuminant, of argon, of anaesthetics, of boiler incrustations and deposits, of bronze powders, of chemical affinity, including equilibrium, catalysis, etc., of casein, of synthetic camphor, of Taylor's

electric furnace process for carbon disulphide, and numerous other substances. Moreover, a large amount of new material has been introduced into the old articles, so that the final effect has been the practical rewriting of nearly the entire book. Also many new illustrations are introduced. Perhaps the largest amount of new material added occurs in the article on "Analysis" which has been increased from 56 to 101 pages, of which 16 pages are devoted to the new field of Electrochemical Analysis, including many illustrations of the various appliances devised by Classen, E. F. Smith, F. M. Perkin, Frary, Gooch, and others.

Copious references to the more recent work of chemical investigations brings the data up to about the end of 1910, and much of the older out-of-date matter has been eliminated. Although most of the articles are by British authors, considerable attention is devoted to American practice and many references to American journals and publications increase the value of the work to users in this country.

The general plan of the original publication has been retained in this edition: the arrangement of subjects is alphabetical, with cross references in all cases which may be classed under different heads. Notwithstanding collaboration of so many authors, there is general uniformity in nomenclature, abbreviations, references, weights, etc., evidencing much care here also on the part of the editor.

The make-up of the book is very satisfactory, with clear print on heavy paper, and strong cloth binding suitable for the hard usage which reference books must endure. The proof-reading has been very carefully done and this new issue will at once meet favor as a standard reference work.

F. H. THORP

DIE CHEMIE DER CELLULOSE, unter besonderer Berücksichtigung der Textil- und Zellstoffindustrien. VON DR. PHIL. CARL G. SCHWABER, a.o. Professor an der Grossh. Techn. Hochschule zu Darmstadt. Zweite Hälfte (Schluss des Werkes). Berlin: Verlag von Gebrüder Borntraeger. 1911. pp. xii + 273-665. Price, M. 14.80.

In the first 90 pages of this half the discussion of cotton cellulose is continued from the previous half, its esters, nitrates,

acetates, viscose, etc., as well as its decomposition products and constitution, being taken up.

From this point on the subject matter is more varied, including information relating to the compound celluloses, the technical preparation of raw materials, the celluloses separated from the raw materials, etc. There is also a short section devoted to the mercerization of cotton, artificial silk manufacture, the treatment of rags for paper stock and the preparation of parchments and vulcanized fiber. The final section is devoted to the analytical methods, both qualitative and quantitative, which are used in cellulose chemistry.

The book closes with an introduction and table of contents and an alphabetical index, both by authors and subjects, covering both parts. The arrangement of the work is, in general, excellent and the indexes are good, especially that of authors' names. The subject index could have been rather more detailed to good advantage but when used in conjunction with the contents little trouble is encountered in locating any desired statements. The typography is pleasing and but few errors are observed, among those noted being two on p. 518 where the yield on the absolutely dry basis is given as 24 per cent. for *P. alba*, while for the figures given it should be 35 per cent. Toward the bottom of the page the scientific name of hemlock is given as *Tanga canadensis* while it should be *Tsuga canadensis*.

This volume presents the chemistry of cellulose up to the date of its publication and covers the ground with remarkable thoroughness. The care which the author has used in reviewing the literature of the subject is evidenced by the presence of over fourteen hundred references to original articles in this half.

There are of course statements in this book to which some will take exceptions, but in the reviewer's opinion it is by far the best work on the subject and should be in the hands of all who are interested in any way in the chemistry or technics of cellulose.

E. SUTERMEISTER

THE CHEMISTRY OF BREAD-MAKING. By JAMES GRANT, M.Sc. TECH., F.I.C., F.C.S., Head of the Fermentation Industries Department in the Municipal School of Technology, Manchester; Examiner in Chemical Technology in the Victoria University, Manchester. With plates. New York: Longmans, Green & Co. London: Edward Arnold. 1912. pp. vii + 224. Price, \$1.40.

The author states in the preface that this book "is put forward in the hope that it may fill a gap which undoubtedly exists in the literature and text-books on this subject." Its contents, however, show a surprising lack of familiarity with recent excellent contributions to the literature on the chemistry of wheat and its products, particularly those which have been published in this country. Apparently the writer is ignorant of the large mass of material which has been presented in the bulletins and reports of the Agricultural Experiment Stations, during the past ten years.

The first 100 pages of the book are devoted to a review of some of the elements of physics and chemistry, and the next 50 pages to the mechanics and biology of milling and baking. It is the author's recommendation that these be studied "in conjunction with some simple text-books on chemistry, physics, mechanics, and the elements of biology and botany." It is the reviewer's opinion that the chapters on these subjects add little to the material which would be found in such text-books and that the questionable application of some of the matter here presented to the field of bread-making will tend to confuse rather than clarify the situation, in the minds of readers unfamiliar with these sciences.

The book contains many statements which, in the light of the positive results of recent researches, must be considered as inaccuracies. These are particularly noticeable in the discussions of the distribution of starch and proteid matter in the wheat berry, of the nature and functions of glutenin and gliadin and of the nature of color and other properties of flour. The chapter on the "Organic Constituents of Cereals" contains rather elaborate descriptions and formulas for various hydroxy acids, an excellent summary of the composition of fats, with formulas and reactions for saponification, but a very incomplete discussion of the proteids; giving properties

and structure only of asparagine, a compound not found in ordinary cereals.

The plates which are reproductions of photographs of portions of the wheat, flour and berry are excellent, but the diagrams intended to represent different parts of the wheat plant are very poor. The sketch of wheat berries, on page 97, would scarcely be recognized as such by anyone who has ever seen wheat grains, and certainly would convey a very inadequate impression to one who has not.

The book abounds in English terms which are unfamiliar, if not unintelligible, to an American reader. In general, it may be said that, while the purpose of the writer in preparing the book is highly commendable, the book itself is hardly to be regarded as a valuable contribution to the literature of the subject, at least for American readers.

R. W. THATCHER

AN EXPERIMENTAL COURSE OF PHYSICAL CHEMISTRY. Part II. Dynamical Experiments. By JAMES FREDERICK SPENCER, D.Sc. (Liverpool), Ph.D. (Breslau), Assistant Lecturer of Chemistry, Bedford College (University of London), Fellow of Victoria University. London: G. Bell and Sons, Ltd. 1911. pp. xvi + 256. Price, 3 s. 6 d.

The appearance of Volume I of this book has already been noticed in *THIS JOURNAL*.¹ Says the author: "Owing to the large number of chemical students who are insufficiently grounded in physics, it has been deemed well to describe, in detail, methods of measuring the electrical quantities, resistance, capacity, electromotive force and dielectric constant in the chapters where the physical chemical relationships of those properties are discussed." This is certainly a wise mode of procedure.

The choice of experiments throughout this volume is excellent, and the descriptions for the most part adequate and satisfactory.

About the only adverse criticism is that a love for the antique still manifests itself, especially in the migration velocity apparatus on page 81, which has been superseded by far better forms.

H. C. J.

¹ Vol. 48, p. 649.

DIE METHODEN DER MASSANALYSE. Zugleich 8. völlig umgearbeitete Auflage von Fr. Mohr's Lehrbuch der chemisch-analytischen Titrimethode. VON DR. H. BECKURTS, Geh. Medizinalrat, o Professor und Vorstand des pharmaz.-chemischen Instituts der Technischen Hochschule Braunschweig, unter Mitwirkung von Dr. O. LÜNING. Zweite Abteilung. Mit 111 eingedruckten Abbildungen. Braunschweig: Druck und Verlag von Friedr. Vieweg und Sohn. 1912. pp. v + 360. Price, M. 10.

The nature of this extensive work on Volumetric Analysis was discussed in the review of Part I.¹ Part II deals with oxidation and reduction processes, with a critical review of the literature and descriptions of the more generally accepted methods. It includes the determination of a number of the rarer elements, as cerium, lanthanum, didymium, niobium, etc., as well as a large number of organic analyses of different kinds. The numerous references cover the literature through 1910. The final volume (Part III) is in press and will complete a work that should be of great value to the analyst, not only as an index to the literature but also as a source of concise information with regard to special analyses.

R. S. WILLIAMS

E. MERCK'S ANNUAL REPORT OF RECENT ADVANCES IN PHARMACEUTICAL CHEMISTRY AND THERAPEUTICS. 1910, Volume XXIV. Darmstadt: E. Merck. 1911. pp. 419.

Of the present volume of the "Annual Report," 38 pages are given to the "Cacodylates and their Therapeutic Uses," and 25 pages to Kephir, then follows the usual report on Preparations and Drugs. Especially interesting at this time is the section on Salvarsan, with its 250 or so references to the literature.

C. A. R.

PRÜFUNG DER CHEMISCHEN REAGENTIEN AUF REINHEIT. VON E. MERCK. Zweite Auflage. Darmstadt: E. Merck. 1912. pp. v + 332.

Few changes have been made in the second edition of this very useful book, except that new reagents which have come into use since the appearance of the first edition in 1905, such as benzidine, dimethylglyoxime, nitron, have been included, together with references to the literature bearing on them.

C. A. R.

¹ THIS JOURNAL, 48, 89 (1911).